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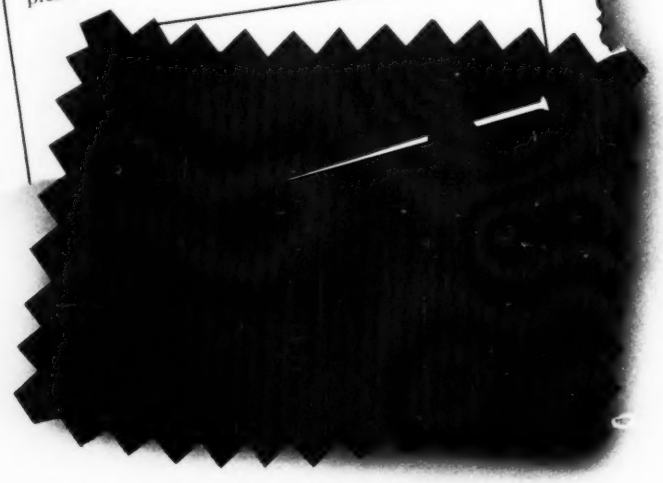

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AMERICAN

DYESTUFF REPORTER

VOLUME 43 NOVEMBER 8, 1954 NUMBER 23

SULFONATION—SULFATION*

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J P Sisley

INTRODUCTION

THE aromatic hydrocarbons react easily with sulfuric acid or its derivatives to form sulfonic acids. This reaction in combination with nitration made it possible, more or less up to 1892, to distinguish between the aromatic hydrocarbons and the acyclic hydrocarbons. As a matter of fact, in the fatty series, with rare exceptions (trimethylacetic acid, acetylene, etc) sulfuric acid does not form sulfonic acids.

Sulfonic acids are remarkably strong acids. The monovalent group SO_3H, which is characteristic of them, contains a hexavalent sulfur atom. Various workers have derived aryl sulfonic acids from sulfurous acid. Benzene sulfonic acid has been called phenyl sulfurous acid. This seems logical since sulfurous acid and the arylsulfonic acids give out a Raman ray of the same frequency.

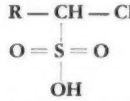
The Commission of Liege in 1930 approved the name "sulfonic", specifying that "sulfonic acids shall be designated by adding to the name of the hydrocarbon the suffix sulfonic".

The reaction between certain organic aromatic compounds and sulfuric acid gives rise to the formation of water-soluble sulfonic acids that are stable in the presence of mineral acids.

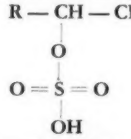
Before studying the new methods of sulfonation, it will be well to consider briefly some generalities of organic chemistry so that we may distinguish between true sulfonated compounds and compounds that are more or less sulfated, or complexes formed by the action of sulfuric acid or one of its derivatives on an organic compound.

In the first place, it is necessary to distinguish between sulfonated derivatives and sulfated compounds which are often confused with them under an ambiguous designation.

A sulfonated derivative is a body having in its molecule a radical $—HSO_3$ in which the hexavalent sulfur atom is attached directly to a carbon atom in the principal chain:



On the other hand a derivative called "sulfated" also contains a $—SO_3H$ group, but the hexavalent sulfur atom is attached to an oxygen atom in the principal chain:



Under normal conditions of treatment, the action of sulfuric acid on the triglycerides leads to formation of "sulfated" derivatives. Mercer and Greenwood, in 1847, took out a patent for a "sulfated" product, while Procter *(1)* suggested that sulfonated castor oils ought to be called sulfated oils.

A sulfated product is, in fact, an alkaline salt of a sulfuric acid ester. As the functional ester is less stable to hydrolysis, it seems better, in order to obtain products having good resistance to hard water and stable to acids, to make the sulfonates.

It is quite evident that the various raw oils react differently with sulfuric acid. On this account, it is necessary to determine the most favorable conditions for obtaining the best effect with each oil.

SULFONATION OF FATTY MATTERS OF ANIMAL AND VEGETABLE ORIGIN ——— Sulfonated oils are remarkable not only because of the variety of raw materials available, but also because of the number of substitutions that are possible to arrive at the same commercial brand.

HISTORICAL

In 1831, Fremy studied the action of sulfuric acid on olive oil, oleic acid and almond oil. He indicates that other workers have been interested in this question before him.

According to Depierre (Traite de la Teinture et de l'Impression), it was Papillon who, in 1790, used a mixture of olive oil and sulfuric acid as a mordant.

The technical employment of sulfonated oils, the first chemical transformation of the fatty acids, dates from 1834; Runge in his book "Chemie des Couleurs" (Chemistry of Colors) reports the use of sulfoleate to replace "huile tournante" (rancid castor oil) in the dyeing of madder. The centenary of Runge's discovery was celebrated in Oranienburg in 1935 *(2)*.

In 1836, two Frenchmen, Dumas and Pelligot, described the sulfuric and phosphoric esters of cetyl alcohol.

John Mercer in 1846 recommended Sulfated Oil A, an olive oil treated with sulfuric acid, as a mordant for dyeing madder.

Gros, Roman, Marozeau and Company, textile printers in Wesserling, used sulfonated olive oil and other sulfoleates for printing fabrics with aniline colors in 1860 *(3)*, while in 1864 Schutzenberger recommended the use of sulfoleic acid in printing aniline black.

However, it was not until 1875 that several colorists manufactured "turkey red oil" from castor oil. Koechlin introduced it at Wesserling while Crum used it in Glasgow.

A more complete study will be found in the report of the Commission of the

* Presented before the Maison de la Chemie in Paris, France in April, 1954.

Societe Industrielle de Mulhouse *(4)* and in a book by Erban *(5)*.

Procter was probably the first to have reported the use of the sulforicinates in the tanning industry in 1890 *(1)*.

The next development came with the introduction of Monopol oils and soaps, patented by Stockhausen *(6)*, products having increased stability toward salts of lime and magnesia and to dilute acids. In 1904, Stockhausen conceived the idea of making soluble compounds containing volatile solvents for degreasing wool.

It is interesting to note that Grun and Woldenburg, in 1909, studied the reactions taking place when castor oil and ricinoleic acid are treated with concentrated sulfuric acid and chlorosulfonic acid *(7)*.

In 1911 Grun described the preparation of a sulfonated derivative of castor oil containing a high percentage of combined SO_3, by the action of chlorosulfonic acid on castor oil in the presence of a solvent *(8)*.

From 1911 to 1925 numerous articles were written on the treatment of different animal and vegetable oils with sulfuric acid. Hilditch's book on sulfated oils *(9)* gives an extensive bibliography on this subject.

In 1925, an important development in the field of surface-active agents started with the introduction of Nekal, an isopropylnaphthalene sulfonate.

A Van der Werth and F Muller in their book *(10)* mention more than 800 patents granted on the sulfonation of oils, fatty acids, aromatic hydrocarbons and on derivatives of these.

More recently Sisley compiled the Index des Huiles Sulfonées et Detergents Modernes, of which the second volume is just off the press.

MECHANISM OF SULFONATION

I—Sulfonation of Lipides and Their Derivatives

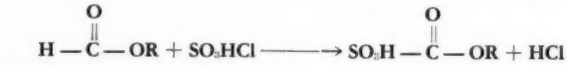
Many studies have been made to determine the changes which fatty bodies undergo on treatment with sulfuric acid. Castor oil, neatsfoot oil, olive oil, peanut oil and fish oils have attracted the attention of research workers on sulfonation, but rapeseed corn and cotton seed oils have received less attention.

Let us consider briefly the reactions that take place in the course of sulfonation of derivatives of fats; alcohols, amines, amides, etc.

A) THE ACTION OF SULFURIC ACID ON SATURATED FATTY ACIDS. ———It is generally agreed that sulfuric acid has no action on saturated fatty acids since they contain no double bonds. However, sulfuric acid can react on saturated hydroxyacids, and under certain conditions it can decompose them.

The introduction of sulfonic groups into a saturated chain can be accomplished by subjecting to the action of SO_3 gas in the presence of solvents *(11)*; by the action of chlorosulfonic acid or SO_3 gas on the melted fatty acid *(12)*; by refluxing with SO_3 in a solution of fatty acid in carbon tetrachloride *(13)*.

L Bert and M Procofieff of the Societe Sinnova *(14)* have discovered that the —O—SO_3H group can be introduced into a saturated fatty acid by starting with the alkyl formate. The reaction proceeds in two stages:



The unstable formate splits up into alkyl sulfate and carbon monoxide:

The reaction can be combined in a single equation, thus:

By the use of Sulfan B, A Sterton and J Weil *(15)* have been able to prepare sulfonated derivatives of various tallow fatty acids, using the method devised by E Gilbert *(16)*.

Disodium α-sulfo palmitate is a surface-active agent of low cost and high resistance to hard water, but having limited solubility; addition of alkaline detergents is necessary in order to obtain washing compounds suitable for laundry use.

B) THE ACTION OF SULFURIC ACID ON UNSATURATED FATTY ACIDS HAVING ONE DOUBLE BOND. ———This subject has been made the goal of many noted research workers, namely Fremy, Muller, Liechti and Suida, as well as the Russian chemists Sabanyeff, Saytzeff, Sukoffet, Schestakoff, de Benedikt, Lewkowitsch, etc.

In the case of the triglycerides, there is partial liberation of glycerol before any other action occurs on the chain.

The first reaction is the fixation of a sulfuric acid ester group at the double bond:

and at the carboxyl group:

These two esters are not too stable, especially the second one. Hydroxylated fatty acids are formed —CH(OH)—CH_2— which are ready to react anew with the sulfuric acid to form sulfuric acid esters.

C) ACTION OF SULFURIC ACID ON UNSATURATED HYDROXY-ACIDS.———The treatment of castor oil leading to production of sulforicinates, Monopol oils and soaps, has given rise to important research work on the part of Scheurer-Kestner, Woldenberg, Grun, Nishizawa, P Juillard, etc.

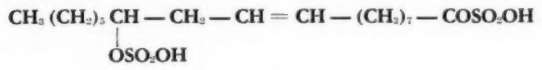
The reactions are multiple and may be schematized thus (see formulas on opposite page):

1) *Scission of the triglyceride leading to the liberation of ricinoleic acid, which combines to give polyricinoleic acid sulfonates free from glycerin.*
2) *Reaction of the sulfuric acid on the hydroxyl group.*
3) *Reaction of the concentrated sulfuric acid on the double bond.* This reaction takes place only when the operation is carried out at low temperature.
4) *Reaction of the sulfuric acid on a CH_2 group.* This reaction results in production of a sulfonic acid, but it takes place only in the presence of dehydrating agents and under special conditions of sulfonation:
5) *Formation of oxyacids.* The reaction leading to the sulfuric acid ester formed on the OH group is reversible and reforms ricinoleic acid, but in the presence of excess of acid or by too rapid sulfonation dioxyacids may be formed.
6) *Formation of complex oxyacids.* By condensation of two or several molecules of ricinoleic acid, polyricinoleic acids are formed by dehydration between the hydroxyl group of one molecule and the carboxyl group of another molecule.

The dehydration may repeat itself to give polyricinoleic acids susceptible to sulfonation forming the complex oxyacid sulfonates that were described by Juillard and Scheurer-Kestner.

7) *Formation of Lactones, Lactides and Estolides.* These reactions are chiefly produced by heating or by dehydration of the sulfonated derivatives of castor oil.

ACTION OF SULFURIC ACID ON UNSATURATED HYDROXYACIDS



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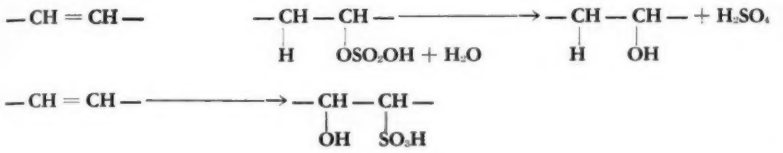
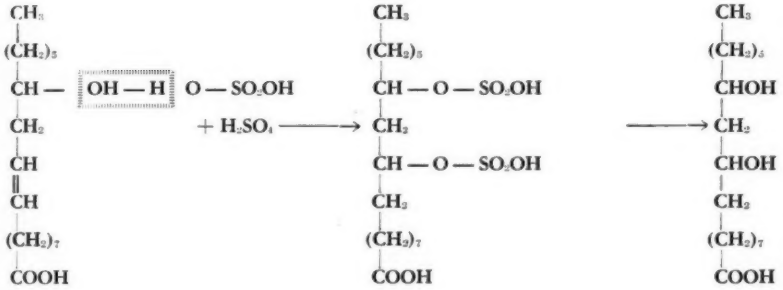


Reaction #3

Reaction #4



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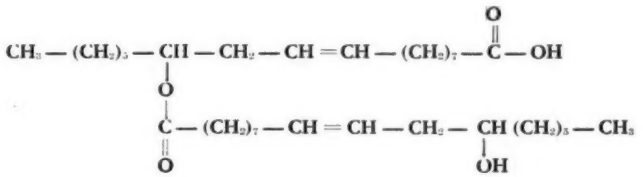
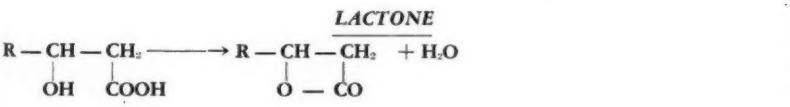


Reaction #6



Reaction #7

The properties of sulfonated oils are influenced by the conditions obtaining during the operations of sulfonation and the time elapsing between the end of the sulfonation and the salt or Glauber salt wash.

The concentration and temperature of the saline solution affect the final sulfonated product as well as the final neutralization. It is therefore necessary to know the transformations that can take place during the course of these operations, the principles of which are discussed in the following paragraphs.

The manufacture of sulfonated oils has furnished the basis of numerous articles *(17)* during the past few years. Contrary to expectation, the development of synthetics has not affected the tonnage manufactured.

Diena *(18)* published in 1949 the results of work on this branch of anion-active compounds, while the equipment and precautions that are necessary to successfully sulfonate oils were the subject of an article which appeared in *Soap, Perfumery and Cosmetics (19).*

There are to be found in the articles of Nishizawa *(20)* pertinent details regarding the influence of the methods of washing and neutralization on sulfonated oils as well as on the mechanism of sulfonation.

II Sulfonating Agents

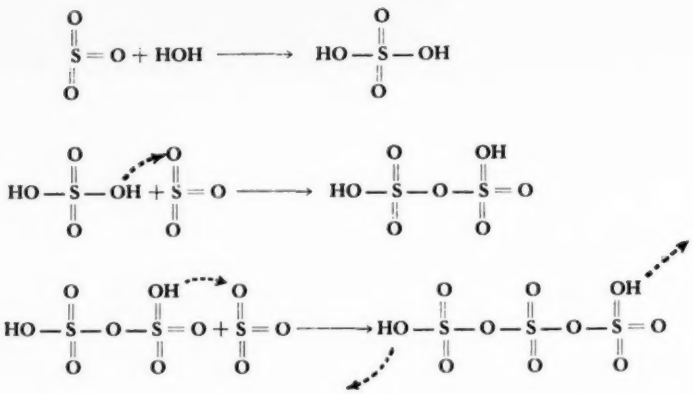
Sulfuric acid, 66° Bé, containing 100% active ingredient, 20% oleum and chlorosulfonic acid are the agents most commonly employed for sulfonation and sulfation.

Sulfuric anhydride (sulfur trioxide, SO_3) is theoretically the most active reagent for sulfonation, but its destructive action on organic matters and the violence of its reaction have limited its use to reactions in which it can be employed in a diluted form with inert solvents. Its instability is likewise a limiting factor.

The General Chemical Company, a division of Allied Chemical & Dye Corporation, has a method of stabilizing sulfuric anhydride by adding less than 0.5% of a stabilizer. The product is sold under the name of Sulfan. The manufacture of this material is being carried on in France by the Kuhlmann Company.

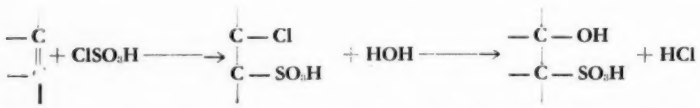
The interesting thing about Sulfan is that it retains its liquid form and can be diluted in a solvent or in an inert gas so that the rate of sulfonation can be controlled as desired. It is more economical to use and much more manageable than ordinary SO_3, when used in the form of oleum, on account of the extra cost of the sulfuric acid.

Sulfan must be carefully handled and not allowed to come in contact with atmospheric moisture, otherwise polymerization takes place leading to formation of the beta form of SO_3:

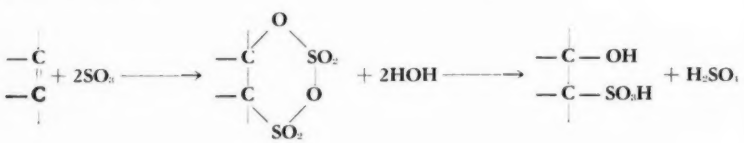


In the case of polymerization of ordinary SO_3, the mechanics of the reaction are the same, but the solid complexes of the alpha form which are obtained have a higher degree of polymerization and a higher melting point.

Sulfan has been recommended for the sulfonation of lipides in order to obtain sulfonates having a higher combined SO_3 content and higher resistance to acids. Analogous products may be made by using chlorosulfonic acid, which reacts according to this equation:



In the case of Sulfan the reaction takes place in this way:



As the equation shows, the carbyl sulfate hydrolizes giving the same hydroxysulfonate as with chlorosulfonic acid.

When Sulfan is used, sulfuric acid is formed in place of the much more corrosive hydrochloric acid. The injurious action of the liberated hydrochloric acid on the apparatus is avoided. In some cases chlorosulfonic acid may cause fixation of chlorine on the organic material being treated.

The advantages of using this stabilized sulfuric anhydride has been emphasized in the literature, especially for sulfonating oils, fatty alcohols, amides, ethanolamides and alkylates *(21)*. A good review was made by E Gilbert and P Jones in an article on sulfonation and sulfation in 1953 *(22)*. A good article on this subject appeared in the Bulletin d'Information de L'ITERG *(24)*.

Technical discussions have been presented by E Gilbert, B Veldhuis, E Carlson and S Giolito *(23)*.

One of the characteristics of the rapid evolution of the saponides is that every soapmaker is potentially a manufacturer of synthetic detergents. This circumstance makes a convenient outlet for the manufacture of raw materials for making detergents. The Continental Oil Company set up a pilot plant for sulfonation of dodecyl benzene as an aid in selling this compound. This is a veritable miniature synthetic detergent plant including a complete industrial-type sulfonating apparatus, with all the side services required, including a well-equipped control laboratory.

The advantages, both economic and technical, accruing to such a pilot installation have been recognized in France where the Kuhlmann Company, at their chemical works at Madelaine-le-Lille, have set up a similar pilot plant for sulfonation and sulfation. It is designed to accomplish these operations by means of Sulfan.

The Sulfan is carried into the apparatus by means of a current of dry air. The concentration of Sulfan in the air varies according to the type of compound being sulfonated (fatty alcohols or alkenes) and its concentration is limited only by the efficiency of the refrigeration system.

The sulfonator consists of a closed cylindrical vessel supplied with a helicoidal agitator. It can be heated or cooled by means of a double jacket and it has also a refrigerating coil with attached pump, which doubles the cooling surface of the sulfonator.

The sulfonating vessel is furnished with a sight glass which can be opened to take samples while the apparatus operates at a slight vacuum, which provides a good safety factor.

The quantity of Sulfan required to make a good sulfonation exceeds only by a small percentage the theoretical quantity and varies according to the type of raw material being treated and the temperature.

The neutralizer is a simple tank with agitator furnished with a system of refrigeration in which the sulfonic acids are run into the neutralizing chemicals. The operation is remarkable for its simplicity and flexibility.

The installation is completed by a panel on which are recorders registering the temperatures of vaporization, refrigeration, sulfonation and neutralization. This process is a considerable step forward in sulfonation. It makes possible the manufacture of sulfonates free from salts, having increased water solubility so that more concentrated liquid detergents can be produced.

SULFONATION OF FATTY ALCOHOLS OF HIGH MOLECULAR WEIGHT

Esterification which results in the production of alkyl sulfates is a difficult reaction unless expensive reagents are used. When pure sulfuric acid is employed the esterification is limited, as it is well known that the reaction is reversible. It is necessary therefore to add to the reaction mixture some substance capable of absorbing the water formed (sulfuric or acetic anhydride), or to use a derivative of sulfuric acid.

Among the reagents suggested are sulfuryl chloride, SO_2Cl_2, or the halohyurines, chlorosulfonic acid, SO_3HCl or sulfuric chlorhydrine. The first of these agents is costly, the second requires inconvenient handling, so that it is impossible to avoid the use of monohydrated sulfuric acid or 20% oleum.

In this case, in order to push the reaction sufficiently far, a large excess of acid is used, which causes the appearance of secondary reactions, formation of ether oxides, sulfones, or even more or less polymerized hydrocarbons.

This last reaction may explain certain anomalies in the titer of hydrocarbons in deliveries of sulfonated fatty alcohols. The cosmetic industry in making shampooing compounds is severely critical on this count.

It is worthy of note that difficulties of the same order are encountered when other esterifying agents are used, particularly phosphoric and pyrophosphoric acids.

Loss of yield is avoided by carrying out the operation at low temperatures between 0° and 35°C for relatively sensitive fatty alochols, and between 40 and 55°C

for saturated alcohols higher than C_{14}.

However, on the plant scale, it is not possible to accomplish the complete esterification with all the acid used, as this is intentionally used in excess. In cases where the presence of mineral salts is objectionable, the problem of separating the salt-free ester comes up.

In sulfonation, the matter of quantities of materials is less important than some of the details intimately connected with the process, such as temperature and the efficiency of the apparatus employed. Local over-heating can be avoided by means of ample and efficacious agitation.

The increasing practice of using chlorosulfonic acid (sulfuric chlorohydrine), necessitates removal of the hydrochloric acid formed, either by degassing or by agitation.

Let us consider two typical cases:

1) *Sulfonation of saturated fatty alcohols* (lauryl, myristyl, stearyl and cetyl).
2) *Sulfonation of unsaturated fatty alcohols* (oleyl).

The method may be defined as follows:

a) The sulfonation must be carried out with a sufficient quantity of 98-100% sulfuric acid to obtain a product soluble in water. The quantity varies, generally speaking, between one-half and two-thirds of the quantity of fatty alcohol being treated.

b) The temperature during sulfonation should be as near as possible to 30°C. However, this temperature may be increased according to the number of carbon atoms and the melting point of the fatty alcohol; stearyl alcohol can be sulfonated at 50°C.

c) The operation of neutralization is carried out after the product is found to be water soluble.

d) The mass must be neutralized as quickly as possible, taking care that the temperature does not rise above 30°C and that there is no local over-heating.

Lauryl alcohol gives a very pasty sulfonated product; frequently the alcohol is mixed with a little acetic anhydride in order to make the sulfonation easier.

Cetyl and stearyl alcohols may be sulfonated at 40 to 50°C.

The sulfonation of oleyl alcohol is a more delicate operation. The temperature must be watched very carefully during addition of the first half of the acid. When a high degree of sulfonation is desired it is better to use chlorosulfonic acid. Neutralization is done with caustic soda. The drying of the finished product is somewhat difficult and can only be carried out successfully by adding a large proportion of sodium sulfate and spray drying. In certain cases the problem of separating the sulfuric ester comes into question. This is accomplished by either of two methods:

1) by precipitating as a lime salt followed by filtration and conversion of the lime salt into the sodium salt; or
2) separation of the crude sulfonate by mixing with a solvent, separation of the lower acid layer and elimination of the solvent from the upper layer.

These separations consume a great deal of time and labor, steam and reagents, and besides, they reduce the yield.

For this reason it is necessary to reduce the quantity of sulfonating agent to the least possible amount or to have recourse to other methods of introducing the —O—SO_2OH group when preparing a product low in mineral salts.

Sulfonation of the fatty alcohol in the presence of solvents forms an azeotropic mixture *(25)*, which makes it possible to obtain a yield on the order of 99%.

E Gilbert and E Paul Jones *(26)* in a study of sulfonation and sulfation have noted several different methods of sulfonation of fatty alcohols.

Clark and Malkemus *(27)* have published researches on the sulfonation of fatty alcohols with sulfamic acid, a method previously mentioned by K Markx for making sulfuric acid esters of fatty acid esters *(28)*. They mention the stabilizing effect of additions of alkaline salts and other adjuvants, especially dipotassium tartrate.

The appearance of Oxo alcohols recently put on the market by the Kuhlmann Company brings into consideration the possibility of manufacturing several interesting products starting from these raw materials. This brings to mind the research work done by I G Farben Industries at Leuna in 1943, on the subject of the sulfation of the Oxo alcohols derived from the byproduct of oil-crocking *(29)*.

SULFONATION OF THE SATURATED ALIPHATIC CHAIN COMPOUNDS—— ALKANES

The reaction of hot or cold sulfuric acid with aliphatic chain compounds (alkanes) does not yield sulfonated derivatives. In order to obtain such derivatives it is necessary to form the sulfurylchloride, which is obtained by the combined action of sulfur dioxide and chlorine on the alphatic compound in the presence of ultra-violet rays. The sulfurylchloride compound is then hydrolyzed to form the sulfonic acid, thus:

$$R-CH_2-CH_2-CH_3 + SO_2 + Cl_2 \xrightarrow{\text{U V Rays}} R-CH_2-\underset{\displaystyle SO_2Cl}{CH}-CH_3 + HCl$$

and by hydrolysis:

$$R-CH_2-\underset{\displaystyle SO_2\ Cl+H\ OH}{CH}-CH_3 \longrightarrow R-CH_2-\underset{\displaystyle SO_2OH}{CH}-CH_3 + HCl$$

SULFONATION OF THE ETHYLENIC STRAIGHT CHAIN COMPOUNDS—— ALKENES

Concentrated sulfuric acid readily reacts on the double bonds by simple addition giving sulfated compounds or isethionic derivatives an OH group or only a single H atom being split off from the sulfuric acid molecule, as shown in the following equations:

$$R-CH-CH_2 + HO-\overset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}-OH \longrightarrow$$
$$\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}$$

$$R-\underset{\displaystyle O}{\underset{|}{CH}}-CH_2$$
$$HO-SO_2$$

Sulfate

or

$$R-CH-CH_2 + HO-\overset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}-OH \longrightarrow$$
$$\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}$$

$$R-\underset{\displaystyle OH}{CH}-\underset{\displaystyle SO_3H}{CH_2}$$

Isethionate

Reactions of the sulfate type follow Markownikoff's law.

The secondary alkyl sulfates now on the market are derivatives of the straight chain olefines, C_{12} to C_{18}. They have been the subjects of many articles *(30)*. Stupel particularly has described the manufacture of Teepol *(31)*.

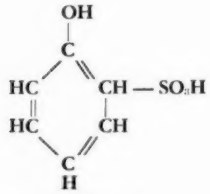
The extremely rapid development of this product in England, in the Stanlow works, and more recently in Holland at the Pernis works, has shown the importance of these surface agents. The Shell-Saint Gobain Company has established a factory at Petit Couronne that is manufacturing 25,000 tons of Teepol per annum. The prime raw material consists of olefines coming from the cracking of paraffin fractions obtained in the refining of lubricating oils.

The cracking is done in such a way as to obtain the maximum yield of olefines of the desired molecular structure, under strictly controlled conditions. The cracking distillates are rectified to obtain the exact fractions required for the sulfonating plant.

The action of sulfuric acid under certain conditions yields products which, after neutralization with caustic soda, give sodium alkyl sulfates. Impurities are removed by a series of extractions with special solvents. The latter are recovered and separated in rectification columns. A train of evaporators treat the purified product and bring it to the desired concentration. *(32)*

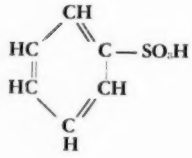
SULFONATION OF AROMATIC HYDROCARBONS

The reaction of sulfuric acid on an aromatic hydrocarbon is simple, and, in some cases, may be carried out in the cold:



Phase I
The isethionic compound on carbon atoms 1 and 2

On Dehydration →

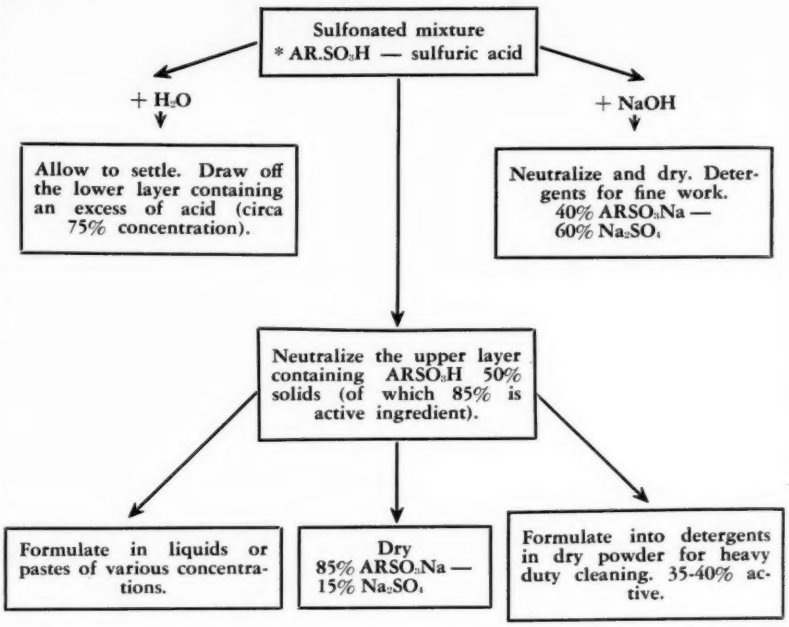


Phase II
On dehydration the sulfonic acid is formed

The sulfonation takes place only in the presence of a dehydrating agent and concentrated sulfuric acid. In spite of the growth of the use of fatty alcohol sulfonates, the alkylaryl sulfonates are the most largely used of the synthetic detergents, since it has been found possible to improve their color and odor. One of the most commonly used of the alkylates is obtained by the reaction of benzene with the tetramer of propylene.

The manufacture of the alkylaryl sulfonates by sulfonation and neutralization of the alkylates is easily adaptable by the soap makers who wish to enter the synthetic field and to make various specialties for various applications. It is interesting to note that the Standard-Kuhlmann Company is selling an alkylate which can be sulfonated, and, at the same time, offering various brands of alkylaryl sulfonates (Stanyl).

FLOW SHEET


Sulfonated mixture
* AR.SO3H — sulfuric acid
+ H2O
+ NaOH
Allow to settle. Draw off the lower layer containing an excess of acid (circa 75% concentration).
Neutralize and dry. Detergents for fine work. 40% ARSO3Na — 60% Na2SO4
Neutralize the upper layer containing ARSO3H 50% solids (of which 85% is active ingredient).
Formulate in liquids or pastes of various concentrations.
Dry 85% ARSO3Na — 15% Na2SO4
Formulate into detergents in dry powder for heavy duty cleaning. 35-40% active.

* AR is hydrocarbon (alkylaryl)

J E Kircher has made a special study *(33)* of the various types of alkylaryl sulfonates and their uses:

a) Household and industrial detergents for fine work containing 40% active ingredient and 60% sodium sulfate.

b) Liquids and pastes of variable concentrations from 25 to 60% active ingredient used as industrial wetting agents.

c) Flakes or granules used principally for industrial purposes.

d) Heavy duty detergents containing 35 to 40% active ingredient to which are added other detergents, phosphates, silicates, sodium carboxymethyl cellulose, optical bleaching agents for home and commercial laundries.

Sulfonation of the alkylbenzenes may be carried out with 100% sulfuric acid (177.5 parts per 100 parts alkylate) with agitation at 20 to 23°C. The temperature is then raised to 40°C and this temperature is maintained for 2 hours.

The mixture is neutralized by pouring it into a 25% solution of caustic soda in sufficient volume to supply 129 kg of pure caustic for each 100 kg alkylate used. The temperature during neutralizing should not be higher than 50 to 55°C maximum. After all the sulfonated product is added the alkalinity and water are adjusted to give a product containing 40% active ingredient.

If a product of 83 to 88% active content is required, 27.5 kg water is added per 100 kg alkylbenzene used, cooling so that the temperature does not exceed 55°C. The mixture is allowed to stand for 1 hour after which the residual acid is decanted off. This acid is about 80% strength, and can be sold for various uses. The supernatant layer is then neutralized to pH 8.0, by addition of a well-agitated solution containing 30 kg caustic soda in 300 kg water. The product obtained is adjusted to the desired strength and alkalinity.

Sulfonation with 20% oleum makes it possible to obtain alkylaryl sulfonates containing 60 to 65% or 83 to 85% active ingredient. 93 kg 20% oleum is used for each 100 kg alkylbenzene.

Very interesting details are to be found in an article by Paulson *(34)* showing a diagram of the installation required as well as graphs that give the important variations in the method of sulfonation which makes it possible to procure an improvement in the whiteness of the product (relation between the amounts of alkylate and acid, percentage of conversion, duration of the reaction and of the decantation).

During the sulfonation of the alkylate, mono- and disulfonic acids are formed and, in addition, a certain amount of sulfones.

As Schwitzer *(35)* has pointed out, the profit margin is hardly sufficient to justify installation of automatic and continuous apparatus by individually owned factories

as it is much more complicated and costly than the relatively simply equipment used in batch processes.

Various articles have been published on this subject *(36)*. Mechanische Moderne offers a continuous sulfonation apparatus based on the Ballestra patent. The device (illustration #5) consists of a double-jacketed autoclave having automatic means of introducing the oleum and the alkylate. The autoclave is an agitator of the turbine type, capable of turning at high speed, which accomplishes immediate and continuous contact of the reagents. A second homogenizing autoclave furnished with four turbine type agitators completes the sulfonation, which takes place at 40°C.

Dilution is done in a third autoclave, where the addition of water is controlled by a constant level regulator.

The diluted mixture is decanted in a conical separator by the florentine vase system.

Neutralization is effected in a fourth autoclave and is regulated by means of an electronically controlled pH meter. The neutralized product is transferred into one of two stock tanks alternately, and in these tanks final adjustments of the finished product are made. Interest in this invention resides in the fact that the apparatus is always under control and that it is easy to stop and restart the sulfonation. This apparatus seems to be particularly well adapted to sulfonation by means of Sulfan. The diluent for the Sulfan is the sulfonation mixture always present in the first sulfonation autoclave.

OTHER METHODS OF FIXATION OF THE —SO_3H and —O—SO_3H GROUPS

There are other methods of fixing the sulfonic group onto an aliphatic chain than by using sulfuric acid, sulfur trioxide or chlorosulfonic acid.

A. OXIDATION METHODS———

1) *By oxidation of the corresponding mercaptans to alcohols or phenols,* which can be accomplished by means of nitric acid:

$$R-SH + O_3 \longrightarrow R-SO_3H$$

Oxidation of disulfides produces analogous results.

2) *Sulfochlorination* of aliphatic hydrocarbons, originally known as the Reed and Horn process, has been the subject of much research and important applications have resulted *(37)*, the Mersolates.

$$RH + Cl_2 + SO_2 \longrightarrow RSO_2Cl + HCl$$

$$RSO_2Cl + 2NaOH \longrightarrow RSO_3Na + H_2O + NaCl$$

3) *Sulfoxidation (38)* is a variation of the sulfochlorination procedure and has been recommended in Germany for the treatment of paraffins and in particular for Mepasine made by the Fisher-Tropsch process. The paraffins are treated with sulfur dioxide and oxygen in the presence of acetic anhydride. In the second phase, the peracetate product is hydrolyzed with water in a reducing bath giving the alkyl sulfonate according to the equations:

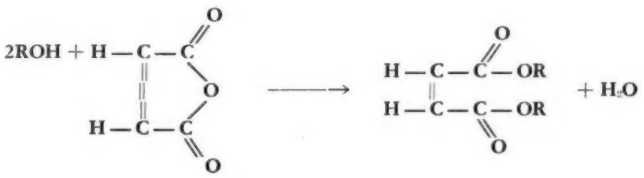
$$RH + SO_2 + O_2 + (CH_3CO)_2O \longrightarrow RSO_2OOCOCH_3 + CH_3COOH$$

$$RSO_2OOCOCH_3 + SO_2 + 2H_2O \longrightarrow RSO_2OH + CH_3COOH + H_2SO_4$$

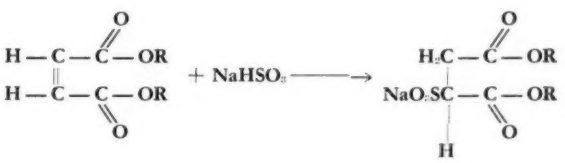
This process, developed by IG Farben Industrie at Hoechst in 1943 has been the subject of many articles *(39)*.

B. ADDITION REACTIONS———

Addition reaction with olefin compound. First the ester of maleic acid is prepared:

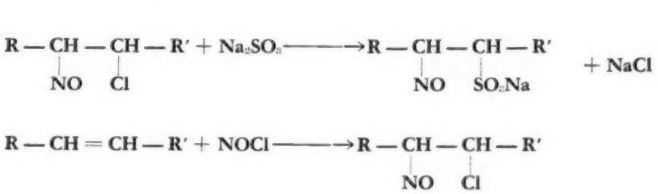


The dialkyl maleate heated with an aqueous solution of sodium bisulfite gives the sulfosuccinate by addition at the double bond:



The monoalkyl maleate may also be used. The resultant product contains both a sulfonic and a carboxyl group. Compounds of this type were described by Caryl and Ericks *(40)* and have been manufactured on a commercial scale by the American Cyanamid Company.

The addition of nitrosyl chloride to a petroleum derivative of the olefin series produces the nitrosochloride, which, on treatment with sodium sulfite, gives a detergent known as Nytron *(42)*. The reactions take place as shown in these equations:



C. SUBSTITUTION REACTION ON THE LIPIDES OR THEIR DERIVATIVES———

1) *Strecker's reaction.* Chloracetyl chloride is caused to react on a hydroxyl group, e g, on a fatty alcohol:

$$C_{12}H_{25}OH + CH_2ClCOCl \longrightarrow C_{12}H_{25} - O - COCH_2Cl + HCl$$

The chloroacetyl derivative, on treatment with sulfites gives the sulfonated compound:

$$C_{12}H_{25} - O - COCH_2Cl + K_2SO_3 \longrightarrow C_{12}H_{25} - O - COCH_2SO_3K + KCl$$

Emargol is a sulfoacetyl compound of fatty acid monoglycerides; Nacconol LAL is sodium lauryl sulfoacetate.

2) *Esterification of fatty acids with sulfonated monovalent alcohols.* By condensing fatty acid chlorides with sodium isethionate, products of the Igepon A type are obtained *(43):*

$$C_{17}H_{33} - COCl + HO - CH_2 - CH_2 - SO_3Na \longrightarrow C_{17}H_{33}COOCH_2CH_2SO_3Na + HCl$$

This compound can also be made by the reaction of the fatty acid on a salt of chloroethane sulfonic acid:

$$R - COOH + ClCH_2CH_2SO_3Na \longrightarrow R - COOCH_2CH_2SO_3Na + HCl$$

This reaction, which has been studied by Tucker *(44)*, is carried out in the presence of mutual solvents, such as the acylamines, at 150°C.

According to Henkel *(43)*, this product can be made by the action of the chloroethyl ester of a fatty acid on sodium sulfite:

$$R - COOCH_2CH_2Cl + Na_2SO_3 \longrightarrow R - COOCH_2CH_2SO_3Na + NaCl$$

Finally it seems possible that this type of compound might be formed by the transesterification of the acetylisethionic ester and a fatty acid of a higher molecular weight.

3) *The Schotten and Baumann reaction.* An important series of anionic detergents is produced by condensation of fatty acid chlorides with the salts of methyl taurine (Igepon T) *(44):*

$$R - COCl + HN(CH_3) - CH_2CH_2 - SO_3Na \longrightarrow R - CON(CH_3) - CH_2CH_2SO_3Na + HCl$$

This type of detergent may likewise be prepared by condensation of fatty amides with chloroethane sulfonate *(45):*

$$R - CONHNa + ClCH_2CH_2 - SO_3Na \longrightarrow R - CONN - CH_2CH_2SO_3Na + NaCl$$

Different fatty acids can be used, e g, oleic, lauric, etc; Igepon TE, a promising chemical product, is being made from the fatty acids of tallow; it is thixotropic, its viscosity increases up to a temperature of 55°C and then diminishes again above that point.

Other reactions may be investigated to produce sulfonated products, among which are sulfo-alkylation, sulfamation, etc.

During the last two years the sale of synthetic surface-active agents has increased 20 to 24% while the sale of soaps decreased 11% in 1953 as against only 6% in 1952. 53% of all sales are synthetic detergents. The production of synthetic detergents in 1952 was 860,000 tons against 725,000 tons in 1951. This production, translated into 100%-active products, amounts to 425,000 tons, of which 182,000 were alkylaryl sulfonates and 47,000 tons were sulfated fatty alcohols. These figures give an idea of the importance of the operations of sulfonation and sulfation that have been discussed in this article.

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Proceedings of the

American Association of Textile Chemists and Colorists

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Editor of Proceedings: Carl Z Draves, 30 Lahey St, New Hyde Park, N Y

NOVEMBER 8, 1954

AATCC CALENDAR

(A general calendar of events may be found on page 772)

COUNCIL
1954—Nov 19 (Hotel Roosevelt, New York).
1955—Jan 21 (Hotel Statler, New York), Apr 15, June 17.

NATIONAL CONVENTIONS
Sept 22-25, 1955 (Chalfonte-Haddon Hall, Atlantic City, N J; 1956 (Waldorf-Astoria, New York); 1957 (Boston).

HUDSON-MOHAWK SECTION
Dec 2, Jan 14, Feb 25, April 15 (Albany, N Y); May 20 (Ladies Night); June 24 (Annual Outing).

NEW YORK SECTION
November 19 (Kohler's Swiss Chalet, Rochelle Park, N J); January 28 (Georgian Room, Hotel Statler, New York); February 25 (Skytop, Hotel Statler, New York); March 18, April 22, May 20 (Kohler's Swiss Chalet, Rochelle Park, N J).

NORTHERN NEW ENGLAND SECTION
Dec 10 (Woodland Golf Club, Auburndale, Mass).

PACIFIC SOUTHWEST SECTION
Dec 3 (Gourmet Restaurant, Beverly Hills, Calif).

PHILADELPHIA SECTION
Dec 3 (Kugler's Restaurant, Philadelphia).

RHODE ISLAND SECTION
Dec 2 (Annual Meeting—Sheraton Biltmore, Providence, R I).

SOUTH CENTRAL SECTION
Dec 4 (Hotel Patten, Chattanooga).

SOUTHEASTERN SECTION
Dec 11 (Atlanta-Biltmore, Atlanta, Ga).

WASHINGTON SECTION
Dec 8 (Pepco Auditorium, Washington); Feb 11 (Washington); May 20.

WESTERN NEW ENGLAND SECTION
Nov 12, Dec 10 (Rapp's Restaurant, Shelton, Conn).

WESTERN NEW YORK SECTION
Nov 27 (Hamilton, Ont); Jan 14 (Buffalo); Mar 4 (Hamilton, Ont); April 22 (Buffalo); June 24 (Outing).

ACTIVITIES OF THE LOCAL SECTIONS

Piedmont

TWO hundred members and guests attended the Annual Meeting of the Piedmont Section at the Wm R Barringer Hotel, Charlotte, N C, on October 16, 1954, following a morning meeting of the sectional research committee, over which Edward A Murray presided.

The afternoon technical session featured papers by Jack Compton, Institute of Textile Technology, on "The Unique Properties of Cyanoethylated Cotton," and Paul B Stam, Dan River Mills, on "A New Chemical Compound for the Stabilization of Viscose Rayon."

Charles H Stone, credited with being "the person most responsible for the founding of the Piedmont Section 30 years ago," was honored at the evening banquet. In recognition of his valuable help during the early years, the officers of the Piedmont Section have created the "Charles H Stone Educational Fund," which will be used to provide financial assistance to students of the textile schools at North Carolina State College and Clemson College.

Other banquet highlights included the installation of officers for 1955; the presentation of a silver tray to Richard Mitchell, in absentia, in recognition of his 25th anniversary as chairman of the Piedmont Section; and the presentation of the past chairman's plaque to Henry A Rutherford, outgoing chairman, by M M McCann.

Newly installed officers include:

Chairman—Herman J Jordan, Piedmont Processing Co

Vice Chairman—Clarence Hooper, Burlington Mills Corp

Secretary—Warren E Rixon, Carbide & Carbon Chemicals Co

Treasurer—Clement O Stevenson, Ciba Co, Inc

Custodian—Arthur R Thompson, Ciba Co, Inc

Councilor (3 years)—Henry A Rutherford, N C State College

Section Committee—George A Artope, National Aniline Div; Jack L Green, Pacific Mills; L E Holt, Burlington Mills Corp; Neal A Truslow, U S Rubber Co.

Western New York

THE inaugural dinner meeting of the Western New York Section, held October 8, 1954 at the Hotel Buffalo, Buffalo, N Y, was attended by fifty-seven members with a large representation from Canada. Honored guests included AATCC president J Robert Bonnar, and Raymond W Jacoby, candidate for the presidency in 1955.

The technical program featured a talk by Henry E Millson, American Cyanamid Co, on "The Effects of Sequestering Agents on Cotton and Wool Dyes."

The members of the Section by majority vote expressed a wish to change the name from Western New York Section to Niagara Frontier Section, as being more representative of its international character. This matter will be brought before the Council at its meeting this month in New York.

—♦ ♦—

Washington

THE Washington Section held its first meeting of the 1954-55 season on October 1 in the lecture room of the East Building of the National Bureau of Standards with approximately 60 members and guests attending.

The speaker of the evening was Jules Labarthe, senior fellow, Mellon Institute of Industrial Research, who discussed "Ten Thousand and One Consumer Complaints and Their Implication for Textile Research and Development."

—♦ ♦—

Rhode Island

APPROXIMATELY 200 members and guests of the Rhode Island Section attended its first meeting of the fall season on October 14 at Johnson's Commodore Room, Providence, R I.

Firth L Dennett, manager, Fiber Treatment Laboratory, Dow Corning Corp, presented a paper entitled "Silicones in Textile Finishing."

THE following members of the AATCC have been elected Fellows of the Society of Dyers and Colourists:

William D Appel, U S Bureau of Standards
Werner von Bergen, Forstman Woolen Co
William H Cady, AATCC
C Norris Rabold, Erwin Mills, Inc.
George L Royer, American Cyanamid Co
Emery I Valko, Onyx Oil & Chemical Co

NOTICE TO SECRETARIES AND PUBLICITY CHAIRMEN OF LOCAL SECTIONS

Papers presented before local sections should be sent to Dr Carl Z Draves, Editor of the *Proceedings*, 30 Lahey Street, New Hyde Park, New York. Authors should provide two copies for this purpose.

Reports of local section meetings should be sent to the American Dyestuff Reporter with copies going to Dr H C Chapin, National Secretary.

Dates of meetings and advance notices of meetings should be sent to the American Dyestuff Reporter with copies also going to Dr Chapin. For publication in any particular issue, information should be in the office of the Reporter 17 days before the issuance date.

EMPLOYMENT REGISTER

This column is open for two insertions per year, per member, without charge. Blanks can be obtained from, and filed with, the Secretary of the Association, Lowell Technological Institute, Lowell, Mass. It is understood that these will be open to inspection by prospective employers who can obtain further information from the Secretary.

54-35

Education: BS, textile institute, textile engg.

Experience: asst designer.

Age: 26; single; veteran; location not restricted.

10-25, 11-8

54-36

Education: MS, textile institute, textile chemistry & dyeing.

Experience: chemist and laboratory manager.

Age: 25; married; veteran; New York or New Jersey preferred but not essential.

10-25, 11-8

54-37

Education: BS, Mass Inst Tech, chemistry.

Experience: chemist with company manufacturing woolens and worsteds since 1921.

Age: 59; married; references; New England preferred but not essential.

10-25, 11-8

Membership Applications

October 22, 1954

SENIOR

Forrest C Ames—Sales engineer, The Wiesner-Rapp Co, Inc, Buffalo, N Y. Sponsors: Earl W Clark, J G Kern.

James R Anderson—Buyer, & assistant buyer of textiles, Sears Roebuck Co, New York, N Y. Sponsors: P J Fynn, G Smith.

Robert S Aries—President, R S Aries & Associates, New York, N Y. Sponsors: L Auer, L L Balassa.

Walter W Arnold—VP, textile machinery engg & sales, The Wiesner-Rapp Co, Inc, Buffalo, N Y. Sponsors: J G Kern, E W Clark.

Bernardo M Barbosa—President, Carlin Mercantile Corp, New York, N Y. Sponsors: E T McIlwain, L Tigler.

John J Cannon—Technical repr, Rohm & Haas Co, Philadelphia, Pa. Sponsors: R G Thomas, H C Borghetty.

David W Chaney—Assistant director of research, Chemstrand Corp, Decatur, Ala. Sponsors: K D Henry, H C Chapin.

Jasper L Collier — Laboratory assistant, Eastman Chemical Products, Inc, Kingsport, Tenn. Sponsors: D G Carmichael, R J Fortune.

Malcolm C Davenport, Jr—Chemist, West Point Mfg Co, Fairfax, Ala. Sponsors: R E Hudson, Jr, A Fisher, Jr.

Anthony V DiPetrillo—General mgr, La Francaise Dyeing & Finishing Co, Paterson, N J. Sponsors: J H Pattman, A B Campana.

Robert M Gaffney—Secondhand, Deering Milliken & Co, Inc, Union, S C. Sponsors: J L Johnson, E J Greene.

John V Geary—Salesman, Ciba, Inc, Boston, Mass. Sponsors: H A Morrison, H X deRedon.

Guido R Genta—Research chemist, National Aniline Div, Allied Chemical & Dye Corp, Buffalo, N Y. Sponsors: J G Kern, E W Clark.

George J Gradel—Chemistry instructor, Philadelphia Textile Inst, Philadelphia, Pa. Sponsors: W H Hughes, P Theel.

John R Hendricks — Production dyer, Delta Finishing Div, J P Stevens Co, Wallace, S C. Sponsors: B F Rivers, C H Payet.

James A Howse — Foreman, Princeton Knitting Mills, Inc, Watertown, Conn. Sponsors: P W Reeves, A W Goodwin.

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William G Wolfgang—Instructor in textile & fiber chemistry, Philadelphia Textile Institute, Philadelphia, Pa. Sponsors: W H Hughes, P Theel.

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JUNIOR

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Robert F Smith—Textile technician, E I duPont de Nemours & Co, Inc, Wil-

(Concluded on page P770)

1st Prize Winner

1954 Intersectional Contest——

SOILING OF FABRICS IN CONTACT WITH THE SKIN*

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A technique for soiling fabrics through contact with the skin has been devised and a quantitative method developed for measuring the accumulated dirt. A series of experiments on rate and degree of soiling in relation to fiber type, fabric structure, and finish show the method to be a convenient and realistic means of studying the factors influencing the accumulation of soil on garments. It has also proved of value for investigating soil removal during laundering and drycleaning.

INTRODUCTION

ALTHOUGH considerable work has been done with carpets and draperies *(1, 2, 3)*, surprisingly little quantitative information is available concerning the rate and degree of soiling and soil removal occurring during everyday use for those fabrics soiled by contact with the skin. While synthetic soils and artificial soiling methods having the virtue of convenience in the laboratory are widely used, the results obtained do not correlate well with natural soiling *(4, 5)*. Thus, until a better understanding of soiling and soil removal is available, studies involving these processes should be performed under realistic conditions. The purpose of this study was to develop a simple, realistic, and relatively rapid method for studying soiling of textile materials in contact with the skin.

Garments are subject to soil from a) the atmosphere, b) contact with soiled objects in the surroundings, and c) contact with the skin itself. The oily secretions of the skin increase the retention of dirt from outside sources. In the regions of the neck, axilla, and groin, skin secretions are at a maximum. Thus, these are frequently the areas of most rapid soiling, particularly when they are also exposed to atmospheric dirt, as at the neck. Secretions of the scalp, cosmetics, and hair dressings also add to the soiling of fabrics in contact with the neck. Since collars are the most rapidly and generally soiled region of a man's shirt, they frequently require special attention in cleaning. Brown *(6)* analyzed the oily constituents which accumulate on a collar and found a variety of fatty acids, neutral fats, and nonsaponifiable materials amounting to about 1% of the weight of the fabric.

A method of soiling was developed utilizing a collar designed to be worn unobtrusively beneath the regular shirt collar. A technique was also worked out for measuring the soil accumulated on the collars employing equipment now in common use in laboratories set up to study soiling and detergency. The "collar method" is believed to approximate the conditions of natural soiling in this region of the body, and should prove useful in the study of soiling and soil removal. Experiments described herein are presented primarily for the purpose of demonstrating the practical application of the method.

Essentially, the "collar test method" used in this study consisted of 1) laundering or drycleaning a collar to remove soil accumulated during manufacture, 2) measuring the reflectance, 3) wearing the collars to soil them, 4) measuring the reflectance, 5) laundering or drycleaning, and 6) measuring the reflectance again. The application of this procedure and the results obtained will now be described in detail.

TEST METHODS

DESIGN AND USE OF TEST COLLARS——The test collars were made according to the pattern shown in Figure 1 from a piece of fabric 18½" long by 3" wide. A plastic stay or stiffener 13" x 1⅛" with round ends made from flexible Saran sheeting was inserted in each collar when support during wear was required. The stiffener was omitted when such fabrics as ladies' dress good were studied.

The test collar was worn inside the subject's regular shirt collar. (See Appendix C). To put it on, the wearer unbuttoned his shirt collar, buttoned one end of the experimental collar onto his shirt button, put the experimental collar around his neck (moving from left to right), and snapped the top snap into the bottom snap corresponding to his neck size. Thus, after the shirt collar was finally buttoned, the experimental collar was in place and did not show above the regular shirt collar. Test subjects found the experimental collar comfortable and in most cases even forgot they were wearing it.

During a series of preliminary studies, experimental collars were given out to different groups of test subjects in the Washington, D C, area. Although some variation was found in the absolute amount of soil depending on whether they worked in an air-conditioned office, in a chemical laboratory, or in an industrial atmosphere, the ranking of the various textile materials was the same irrespective of the group.

It was found that four test collars for each type fabric studied were statistically reliable provided comparative studies were made on the same group of test subjects. For example, in comparing "Fabric A" with "Fabric B" it was desirable to work out a program in which test subject "1" would wear both collars during the period of the test. A fifth collar, which was not worn, was included as a control when soil removal studies were made.

Throughout the experiments described in this paper, collars were always distributed and collected during working hours and on the same day, so that reliable data for the time worn could be obtained. This also provided relatively standardized conditions of wear and made comparisons more reliable.

In Appendix A are presented the original instructions used to carry out the work described in this paper. These may help to provide a program for those interested in performing simliar experiments.

LAUNDERING PROCEDURE——The collars were washed in a cylinder-type automatic home washer. To prevent tangling during washing and to simulate the collar attached to a shirt, each collar was pinned at both ends to a 36-inch square of cotton fabric (new material previously washed twice with a fluorescent-free detergent to remove any soil or sizing). A total load of 4½ pounds in the washer was always used, with additional

* Presented by Daniel Frishman on September 18th in the Empire Room of the Atlanta Biltmore, Atlanta, Ga.

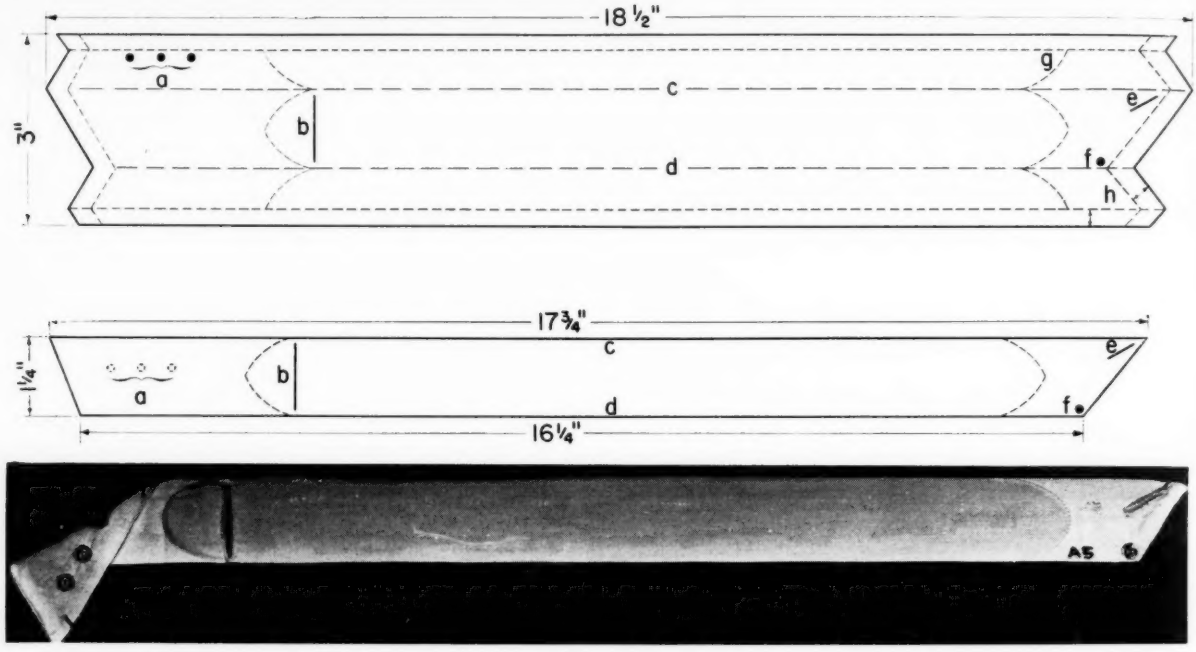

Figure 1
Collar pattern and finished collar

a—Bottom snaps (on outside of collar) for adjusting to 15-inch, 14½-inch, and 14-inch sized collar; b—Slot for inserting stay; c—Fold for upper edge; d—Fold for lower edge; e—Buttonhole for buttoning to shirt collar band; f—Top snap (on inside of collar); g—Stitching line; h—seam allowance (¼ inch).

squares of fabric added when necessary to make up the required weight. Prior to washing, the load was first soaked for 5 minutes at 36°C in 7 gallons of 2° hardness water containing 1.5 tablespoons of detergent, and then extracted. The material was washed with 2 tablespoons of detergent in 5.5 gallons of water at 67°C for 10 minutes, extracted, rinsed at temperatures ranging from 50° to 40°C, and again extracted. The collars were spread on plate glass to dry at room temperature.

To avoid masking the yellowness with the optical brightening agents contained in most household detergents, a detergent prepared in the laboratory was used for all laundering. It included all the ingredients of the typical household materials except for the fluorescent dyestuff. It contained:

55% alkylarylsulfonate, 40% active (inactive material was sodium sulfate)
44% sodium tripolyphosphate
1% carboxymethylcellulose (about 50% active)

STARCHING PROCEDURE———For the starched broadcloth samples, a commercial laundry starch free of fluorescent dye was used. Ten grams of starch were mixed with one tablespoon of cool water and the suspension poured with constant stirring into one cup of boiling water and diluted with one cup of warm water. The collars were wet with distilled water, immersed in hot starch solution for 1 minute, squeezed lightly to remove excess, air dried, dampened, and ironed.

WASHING PROCEDURE———In the study of the rate of soil removal, a different laundering procedure from that described above was used. The collars were pinned to fabric squares and made up to the usual 4½ pound load. Without presoaking they were washed with 1 tablespoon of detergent in water at 40°C for 1 minute, extracted, rinsed without agitation at 40°C for 1 minute, extracted, and spread on glass plate to air dry. Reflectance measurements were made after each of four such laundering cycles.

DRYCLEANING PROCEDURE———Drycleaning was done in Stoddard solvent in a 30" x 30" washer connected to a filter that provided filtration at the rate of 30 theoretical solvent changes per hour in the washer. The solvent in both the washer and the filter contained 4% by volume of a popular drycleaning detergent. The test collars, along with 25 pounds of dresses, were first conditioned at 70°F and 50% relative humidity. They were then placed in the washer and circulation through the filter was started. Sufficient moisture was added to the solvent to maintain the relative vapor pressure of the water in the solvent at 75%. The garments, together with the collars, were agitated in the washer for 30 minutes with the filter circulating solvent through the washer during the entire period. After rinsing 3 minutes in distilled Stoddard solvent, collars and garments were centrifuged to remove excess solvent and then dried in a tumbler with air at 140°F.

MEASUREMENT OF SOILING——— The rate and extent to which fabrics in contact with the skin are soiled, and the effectiveness of laundering and drycleaning procedures in removing this soil, are indicated in this study by changes in both reflectance and color. The instrument used was the Hunter Color Difference Meter (see Figure 2), manufactured by the Gardner Laboratory, Bethesda, Md. It was equipped to give three values for each color measured: "R" or light reflectance; "a," which measures redness when plus, grey at zero, and greenness when minus; and "b," which measures yellowness when plus, grey at zero, and blueness when minus. Other tristimulus colorimeters, such as the Hunter Multi-purpose Reflectometer, the PPG-IDL Color Eye, and the Colormaster Differential Colorimeter can be used in a similar fashion (7, 8).

When the measurements were being made, the plastic stiffener was removed and the collar refolded so that its upper edge ("c" in Figure 1) became the center of the field of view of the instrument (as shown in Figure 3). As denoted by the diamond-shaped areas in Figure 3,

Figure 2
The photoelectric color difference meter

each of three separate areas on the collar was read on the three scales (R, a and b). To obtain the reading, it was necessary to place the collar on a 4" x 5" plate-glass specimen support of the instrument in such a manner that the upper edge of the collar was in the center and parallel to the long dimension of the oval light aperture (2" x 3¼"). In the instrument used the light comes from below, and it was necessary to place the test collar so that its upper edge ("c") was down on the glass plate. The collar was backed and held flattened against the glass specimen support by the white porcelain enamel standard used for balancing the instrument. Because the collar did not completely cover the light aperture, the two beams of light from the instrument were adjusted so that 99% fell on the collar, with 62% of the light convering into a diamond-shaped spot 0.6" x 1.2" at the center of the area.

Reflectance and Color Values Describing Soiling. The "R" value, which measures the total reflectance, is the most widely used method for expressing degree of soiling. Although several derived values describing the change in "R" have been employed, the use of the absolute value has been gaining acceptance recently. Soiling, however, frequently involves a change in hue as well as a reduction in reflectance. This is especially true of materials soiled by contact with the skin. Therefore the "b" values, which when positive indicate yellowness, and when negative, blueness, are used to describe the increase in yellowness. Yellowing of shirt collars with use is a generally recognized fact, although its importance in the study of soiling and detergency has been neglected (*9, 10*).

The "a" values and various derived quantities which indicate change in color (*11*) were much less important to this study and therefore are not reported here.

Calculation of Soil Content from Reflectance Data. Although for practical purposes the change in appearance caused by soiling may be of greatest importance, for studies of soiling and detergency it is also of considerable interest to know the actual amount of dirt present. Many investigators have studied the relationship between actual soil content and reflectance. Bacon and Smith (*12*), applying the formula of Kubelka and Munk (*13*), suggested that the expression

$$\frac{(1-R)^2}{2R}$$

is a linear function of the soil content, where "R" is the reflectance expressed as a fraction instead of as a percentage. Reich et al (*14*) have demonstrated the validity of this expression, especially for low values of soil content. Since the unsoiled fabrics do not have 100% reflectance, Reich (*14*) suggested that the soil content of fabric is actually represented by the formula:

$$\frac{[1-R\ (\text{Soiled})]^2}{2R\ (\text{Soiled})} - \frac{[1-R\ (\text{Original})]^2}{2R\ (\text{Original})}$$

Thus, the term "soil content" in this paper refers to the difference of the two calculated quantities as indicated, and not to results obtained by a chemical analysis for soil. As an aid in interpreting the reflectance data, it should be noted that a decrease in reflectance from 85 to 80% actually represents a smaller accumulation of soil than the change from 75 to 70%. Computation was minimized by preparing a curve relating "soil content" to "R" values from which the calculated results could be read. This graph is shown in Appendix B.

Distribution of Soil on Test Collars. While soiling on the faces of a collar is uniform except for random or accidental streaks, the upper and lower edges are uniformly and much more heavily soiled. A test collar made of cotton broadcloth was heavily soiled by 50 hours' wear and then placed on an optical device (*15*), which was so adjusted as to scan the collar with a pinpoint of light and to record the reflectance continuously. (This measurement gives a picture of the change in reflectance and yellowness.) An examination of Figure 4 (reading left to right) shows that, as one moves from the center of the outside face of the collar, where the reflectance is about 75%, upwards toward the upper edge, the reflectance drops and the yellowness increases slowly. When the edge is reached there is a rapid decrease in reflectance from about 67% down to 46%, and an increase in yellowness. Then as one examines the inside of the collar, moving toward the lower edge, the reflectance is fairly constant at about 64% until the lower edge is reached, where the reflectance drops to about 43%. The yellowness under this same region follows a slightly different trend, indicating a more gradual change. Examination of the outside face of the collar away from the lower edge shows a gradual increase in reflectance and decrease in yellowness. Note that that portion of the curve at the extreme right of Figure 4 is the same as that on the extreme left. The total distance around the collar (from top to bottom and bottom to top) is 2½" and the graph represents this entire distance.

The yellowness values recorded here are in arbitrary units and cannot be compared directly to other values given in this paper. In this instance they are calculated from the formula:

$$\frac{10 \times [R\ (\text{amber filter}) - R\ (\text{blue filter})]}{R\ (\text{amber filter})}$$

The above is simply a means of expressing that fraction of the total reflected light which was found to be yellow.

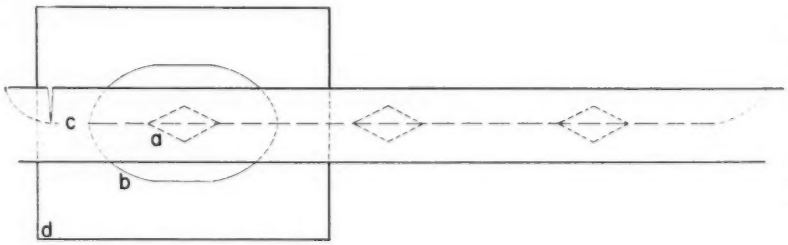

Figure 3
Diagram of collar placed on color difference meter
a—Diamond-shaped light spot and three areas read; b—Oval light aperture; c—Upper edge of collar; d—Plate glass specimen support

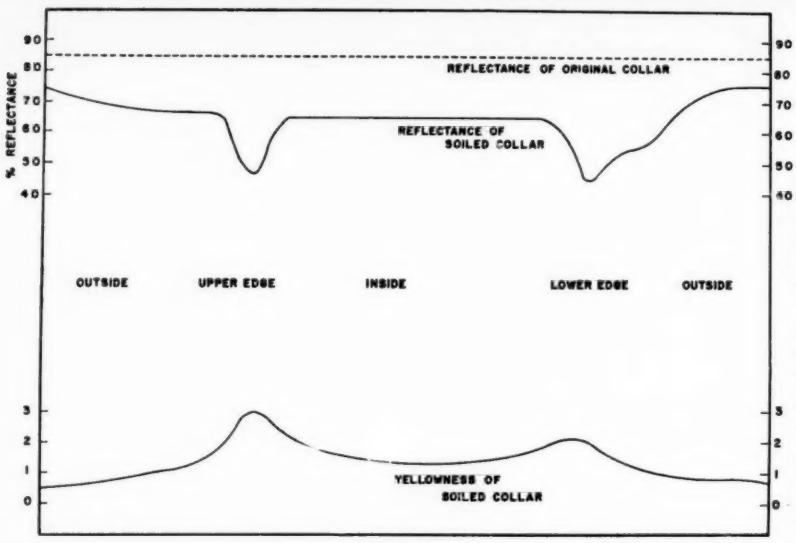

Figure 4
Distribution of soil on a collar

RESULTS AND DISCUSSION

RATE AND EXTENT OF SOILING ——To illustrate the application of the collar technique to a study of soiling, typical white shirting fabrics were evaluated, i e, cotton broadcloth (both plain and starched), cotton oxford, and Dacron. Essentially the method consisted of

1) laundering the collars to remove soil accumulated during manufacture;
2) measuring the reflectance;
3) wearing the collars for a total of 26 hours, in increments of 2-, 3-, 7-, 7-, and 7-hours, and measuring the reflectance after each period of wear; and
4) finally laundering the collars and measuring the reflectance again.

In the case of the group of starched broadcloth collars an additional set of measurements was made after the collar was restarched and ironed. Details of the procedure used are noted in Appendix A.

Changes in reflectance during wear are listed in Table I and shown in Figure 5. The reflectance values show similar trends decreasing with time of wear. When "soil contents" are calculated, thus taking into account differences in initial reflectance, a somewhat different pattern is seen. Figure 6 indicates that the accumulation of soil during wear is essentially linear with time, a result that lends credence to this method of test. Figure 7 demonstrates the rapid increase in yellowness which takes place in the first few hours of wear.

Table I and Figures 5, 6 and 7 indicates that there is little difference among the various cotton fabrics, but that these do differ from Dacron in soiling. Figure 6, particularly, shows that Dacron soils more rapidly.

A survey of the literature shows that there is a difference of opinion regarding

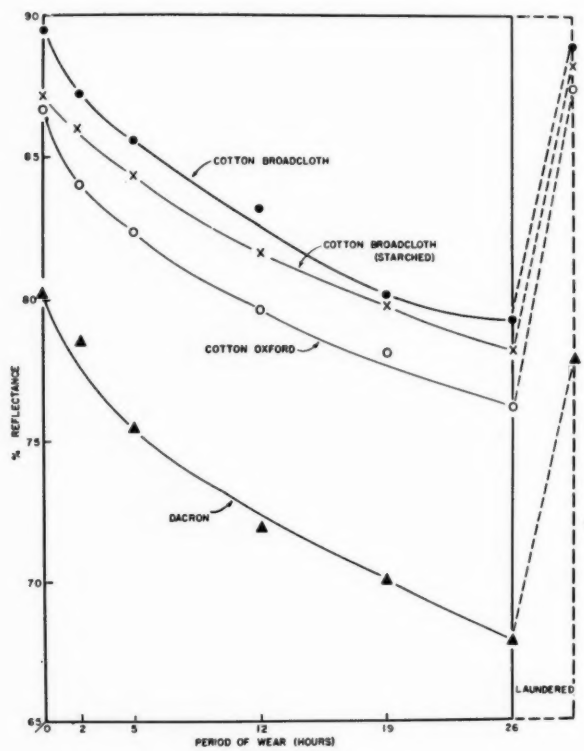

Figure 5
Reflectance as a function of period of wear

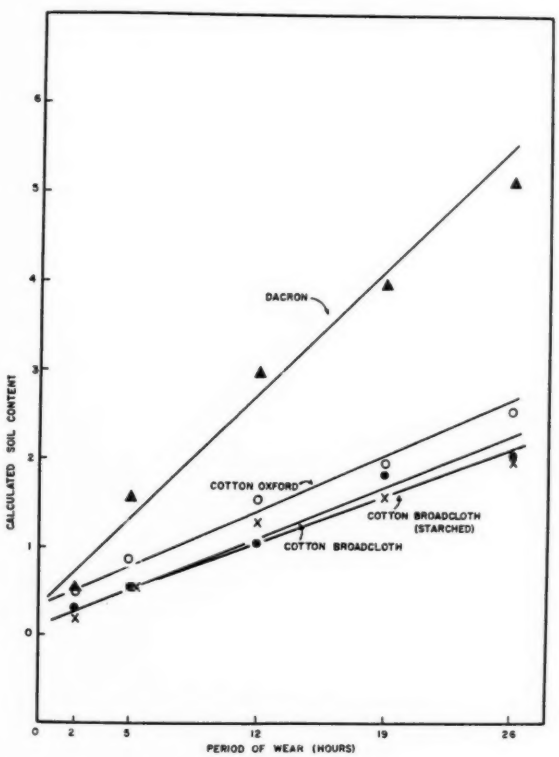

Figure 6
The soil content as derived from reflectance data as a function of the period of wear

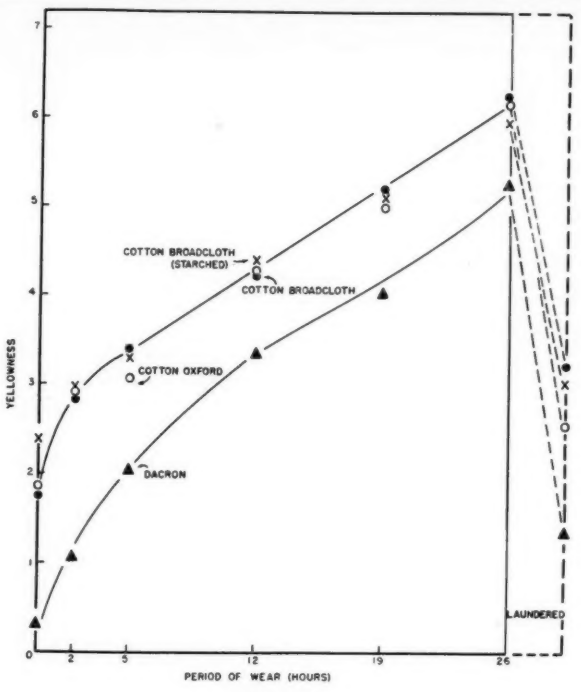

Figure 7
Yellowness as a function of the period of wear

the influence of starch on soiling (*1, 16*). Kruger (*17*) makes the observation that starch makes fabrics more resistant to soiling by forming a more impenetrable surface. The preesnt results indicate that starching effects only a very slight decrease in the rate of soiling. It should be noted that starch, by slightly decreasing the initial reflectance, somewhat minimizes the small advantage gained in decreased rate of soiling.

The greater soiling of the Dacron fabric used in this study is shown by a larger change in total reflectance as well as in yellowness. Initially the fabric is less yellow than the cotton materials, and maintains this position throughout soiling. It is more grey, however, as indicated by its lower total reflectance. The greater soiling of some of the new hydrophobic fibers has been mentioned (*10*). It has been suggested that the oily soils actually "dissolve" within the fiber much as a disperse dye does in acetate.

In a preliminary study, nylon, rayon and cotton broadcloth were compared. The total number of hours of wear for each type of fabric was always the same, but they were worn for various periods of time and were distributed to different groups in the Washington area. The collars were laundered after the required

TABLE I

THE CHANGE IN PERCENT REFLECTANCE, YELLOWNESS, AND SOIL CONTENT AS A FUNCTION OF PERIOD OF WEAR

				Change during wear						
Fabric		*Original values*		*2 hours*	*5 hours*	*12 hours*	*19 hours*	*26 hours*	*Total change laundered*	
Cotton broadcloth	R	89.5	Decrease in reflectance	2.2	3.8	6.3	9.3	10.1	1.0	
	b	1.8	Increase in yellowness	1.0	1.6	2.5	3.4	4.4	1.5	
			Soil content[a]	0.31	0.58	1.07	1.82	2.07	0.64	
Cotton oxford	R	86.7	Decrease in reflectance	2.7	4.2	7.1	8.5	10.6	—0.7[b]	
	b	1.8	Increase in yellowness	1.1	1.2	2.4	3.1	4.3	0.7	
			Soil content[a]	0.50	0.86	1.55	1.95	2.59	—0.13[b]	
										not starched
Cotton broadcloth starched	R	87.1	Decrease in reflectance	1.1	2.8	5.5	7.3	9.0	—0.5[b]	1.2
	b	2.4	Increase in yellowness	0.6	0.9	2.0	2.7	3.6	0.9	0.6
			Soil content[a]	0.21	0.55	1.34	1.59	2.04	—0.17[b]	1.0
Dacron	R	80.1	Decrease in reflectance	1.9	4.8	8.6	10.1	12.3	2.3	
	b	0.3	Increase in yellowness	0.7	1.7	3.0	3.6	4.9	1.0	
			Soil content[a]	0.51	1.58	2.99	3.97	5.16	3.05	

[a] The values given refer to calculated "soil content" as described in the text.
[b] A negative value indicates that the sample is cleaner than before the start of the experiment.

TABLE II

THE REFLECTANCE AND CALCULATED SOIL CONTENT OF NYLON, COTTON AND RAYON FABRICS SUBMITTED TO SUCCESSIVE SOILING AND LAUNDERING

			Wearing time									
			27 hours		*22 hours*		*5 hours*		*2½ hours*		*12 hours*	
Fabric	*Original R*		*Decrease R*	*"Soil Content"*	*Decrease R*	*"Soil Content"*	*Decrease R*	*"Soil Content"*	*Decrease R*	*"Soil Content"*	*Decrease R*	*"Soil Content"*
Cotton broadcloth	88.8	soiled	10.9	2.37	7.2	1.41	6.7	1.30	4.1	0.72	7.1	1.39
		laundered	2.3	0.36	1.8	0.28	1.8	0.28	1.4	0.22	1.6	0.24
Nylon	89.2	soiled	12.7	2.85	11.9	2.31	6.9	1.28	3.8	0.63	9.2	1.86
		laundered	3.6	0.58	3.0	0.48	2.7	0.41	3.0	0.48	4.0	0.66
Rayon	88.6	soiled	11.3	2.51	8.6	1.80	6.3	1.21	6.2	1.19	8.7	1.81
		laundered	2.2	0.35	2.5	0.42	3.8	0.67	3.9	0.67	5.9	1.10

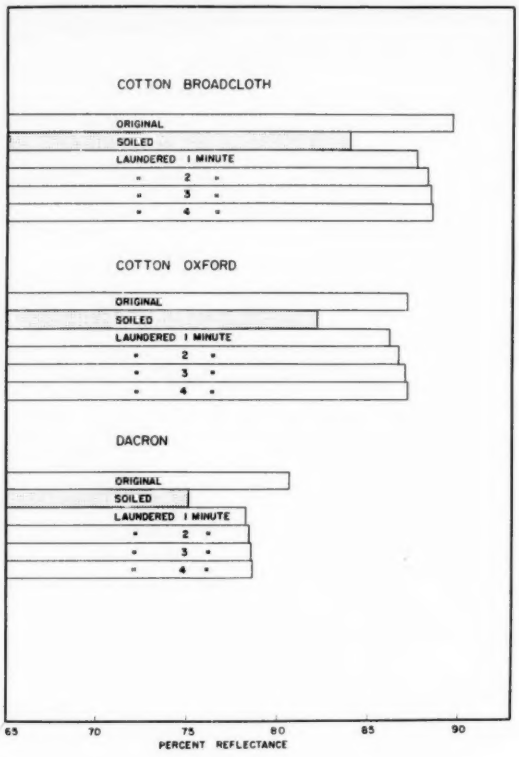

Figure 8
The rate of soil removal during laundering as indicated by reflectance

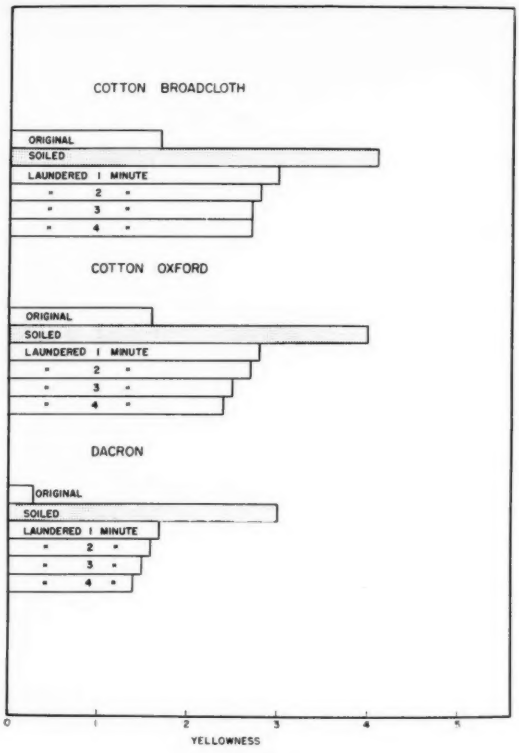

Figure 9
The rate of soil removal during laundering as indicated by yellowness values

number of hours of wear had accumulated. Laundering appeared to bring them back to the original condition and therefore each set could be reliably compared. The results obtained are shown in Table II, the sequence in which the data are presented being the order in which they were worn.

Although nylon had the highest initial reflectance, the apparent order of rank is cotton, rayon, and nylon, with cotton showing the least soil. However it appears that the difference between cotton and nylon is not as large as the difference between cotton and Dacron.

Although the work should be carried further to obtain a wider coverage of present-day fibers, the results described above suggest that this test method can serve as a convenient, practical means for evaluating fabrics with respect to soiling. Furthermore, this technique should serve as a useful guide to those interested in developing soil-resistant finishes as well as to those engaged in fundamental studies of the factors which affect soiling and soil removal.

RATE AND EXTENT OF SOIL REMOVAL IN LAUNDERING——Intensity and period of mechanical action are two important variables in laundering (*12*). In order to demonstrate the use of the soiled collar method for a study of this type, it was decided to evaluate soil removal as a rate processs. The original reflectance of collars made from cotton broadcloth, cotton oxford, and Dacron were measured; the collars were then worn for a period of 26 hours and reflectance measurements again taken. The soiled collars were laundered for four 1-minute periods with reflectance measurements being taken after each period of laundering (see the entire section on "Test Methods" and Appendix A). The results obtained are listed in Table III and illustrated in Figures 8, 9, and 10.

TABLE III
THE CHANGE IN TOTAL REFLECTANCE, YELLOWNESS, AND SOIL CONTENT DURING LAUNDERING

Fabric		*Original value of unsoiled fabrics*		*Change during soiling*	*Changes which take place during laundering compared with original values of unsoiled fabrics*				*Changes which take place on unsoiled fabric after four 1-minute periods of laundering*
					1 min	*2 min*	*3 min*	*4 min*	
Cotton broadcloth	R	89.7	Decrease in reflectance	5.7	2.0	1.4	1.2	1.15	0.9
	b	1.7	Increase in yellowness	2.4	1.3	1.1	1.0	1.0	0.1
			Soil content[a]	0.97	0.25	0.17	0.14	0.13	
Cotton oxford	R	87.2	Decrease in reflectance	5.0	1.0	0.5	0.1	0.0	1.0
	b	1.6	Increase in yellowness	2.4	1.2	1.1	0.9	0.8	0.1
			Soil content[a]	1.01	0.18	0.09	0.01	0.0	
Dacron	R	80.7	Decrease in reflectance	5.6	2.4	2.2	2.1	2.0	1.2
	b	0.3	Increase in yellowness	2.7	1.4	1.3	1.2	1.1	0.1
			Soil content[a]	1.45	0.63	0.57	0.54	0.53	

[a] The values given refer to calculated "soil content" as described in the text.

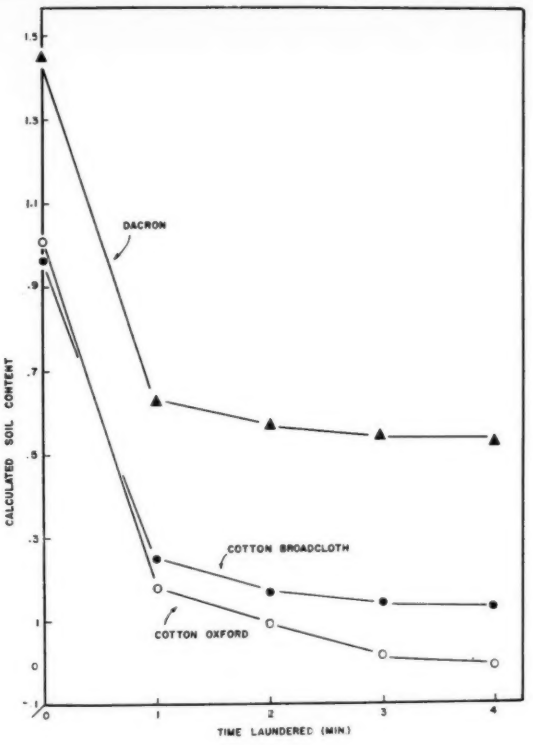

Figure 10
Soil removal during laundering

It is apparent that the greatest amount of soil was removed during the first 1-minute period, and that the total amount of soil removed was approximately the same for the three materials studied. However, the Dacron shirting fabric, having accumulated more soil during wear, also retained more at the end of the laundering process. This is in good agreement with the data given in Table I, which lists results of a more severe washing process. Similarly the results indicate that the behavior of nylon resembles that of Dacron, as shown in Tables I and III. These results are consistent with the hypothesis that some of the oily soil penetrates the hydrophobic fiber and is not easily removed in an aqueous medium. As will be discussed later, drycleaning solvents appear to be more effective in removing oily soils from hydrophobic fibers.

Tables I and III both show that the cotton oxford material loses more soil during laundering than the cotton broadcloth. This difference probably can be attributed to the more open-weave structure of the oxford fabric and to the greater accessibility of soil to the laundering solution. The starched fabric, which was only slightly less soiled than the unstarched material, lost more soil in laundering — a result which can probably be explained by assuming that some of the soil is on the starch and that during laundering the starch is more easily removed than soil.

The Influence of Fluorescent Dyes in Laundering. Optical brightening agents (fluorescent dyestuffs) are now used as a component of most household detergents. Their influence in decreasing the yellowness values, even in an instrument using an incandescent light containing only a small amount of ultraviolet, was made readily apparent in the early stages of this work where a well-known household detergent was used. Collars made of nylon, cotton, and rayon fabric were worn and laundered repeatedly and measured for reflectance and yellowness after each laundering. A group of unsoiled control collars were also laundered at the same time. After five such cycles, the collars were measured with an ultraviolet filter present in the instrument. The results obtained (see Table IV) were consistent with those noted by examination of the collars under an ultraviolet "black" light; the cotton collars strongly adsorbed the fluorescent dye, while the nylon adsorbed only a small amount, and the rayon practically none. The greater adsorption by nylon as compared with rayon is surprising since the dyeing properties of the latter are known to be similar to those of cotton. It appears that the adsorption of fluorescent dye by cotton is almost sufficient to completely mask the yellowness which increases with successive wearings. Laundering of the unsoiled control collars also caused the apparent yellowness to decrease although measurement with the ultraviolet filter showed that it was actually increasing with successive launderings. It was for this reason that the aforementioned specially prepared detergent, duplicating the commercial product except for the fluorescent dyestuff, was used in all subsequent laundering experiments. The formula for this detergent is given in the earlier section on "Test Methods."

SOIL REMOVAL IN DRYCLEANING ——The method was also investigated for its applicability to the study of soil removal during drycleaning. A group of collars made from acetate, rayon, and Dacron fabrics were first drycleaned and measured for reflectance. They were then worn for a total of 26 hours, drycleaned, and measured again for reflectance. The details of the commercial drycleaning procedure using Stoddard solvent are given in the earlier section on "Test Methods."

Reflectance measurements and the calculated values from them are given in Table V and Figure 11. The extent of soil removal from these fabrics by drycleaning was very good, as indicated by the R values. In the case of Dacron, the only sample which can be used for comparison, soil removal in drycleaning ap-

TABLE IV
THE INFLUENCE OF FLUORESCENT DYESTUFF ON YELLOWNESS DURING LAUNDERING

Fabric	Yellowness of original fabric	Number of launderings	1	2	3	4	5	5
			Yellowness after launderings					
			Without UV filter present					With U-V filter
Nylon	4.9	Not soiled	4.9	5.1	5.1	5.1	5.1	5.7
		Soiled before each laundering	6.0	6.3	6.5	6.6	6.8	7.0
Cotton	4.1	Not soiled	3.0	2.9	2.7	2.5	2.4	3.6
		Soiled before each laundering	4.4	4.9	4.9	4.5	4.9	5.9
Rayon	3.1	Not soiled	2.8	2.6	2.8	2.8	2.5	2.7
		Soiled before each laundering	4.0	4.0	4.1	3.8	4.3	4.4

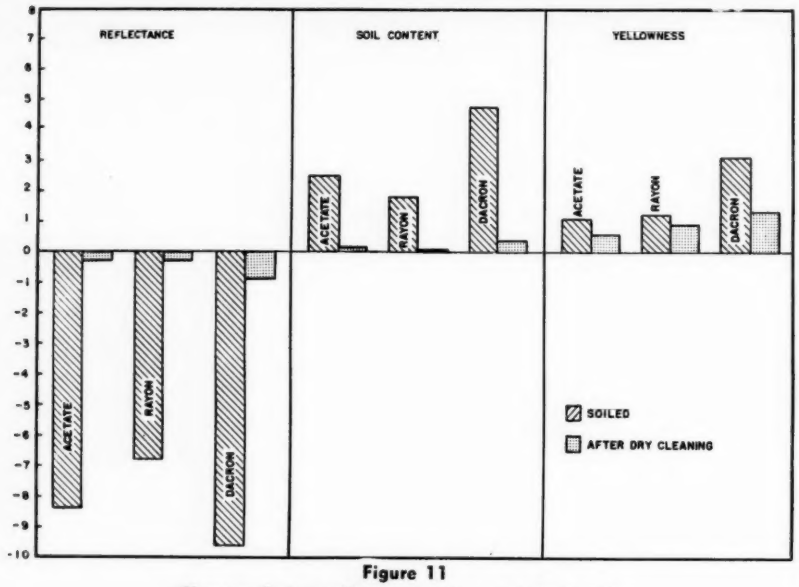

Figure 11
Changes during soiling and subsequent drycleaning

peared to be superior to that in laundering. However, as judged by the results on Dacron, decrease in yellowness was less satisfactory than that in laundering. These results suggest that the yellow stains may consist of materials which are not soluble in the solvent employed.

SUMMARY AND CONCLUSIONS

1) Fabrics that are soiled through contact with the skin represent a very large volume of material regularly laundered or drycleaned. Despite its importance, very little quantitative information is available, and realistic methods for accumulating and evaluating soiling of this type are lacking.

2) A realistic method for soiling a fabric by contact with the skin was devised using a test collar which can be worn unobtrusively under the regular shirt collar; and a technique for measuring the degree of soiling was developed by adaptation of the usual photo-electric optical devices to the determination of reflectance and hue of the test collars. The Kubelka-Munk equation was used to calculate a figure for "soil content," and was found a valuable tool in interpreting test results.

3) The results of a series of experiments used to develop the techniques were presented as a means of demonstrating the application of the method to the study of soiling and soil removal. In determining the rate and extent of soiling and soil removal, the collar test was applied to fabrics made from a variety of fibers. The results of these experiments indicate that:

a) For the particular fabrics studied, cotton appears to soil less readily than nylon and Dacron, while rayon and acetate are intermediate.

b) Minor differences show up in the soiling of cotton broadcloth vs cotton oxford and starched vs unstarched cotton fabrics.

c) While reflectance decreases rapidly at first and then more slowly, the accumulation of soil is linear over the entire period of wear.

d) Yellowness is an important consideration for all fibers in the study of soiling by contact with the skin.

e) The optical brightening agent contained in at least one of the popular household detergents is effective in masking the increasing yellowness of cotton resulting from repeated soiling and laundering cycles.

f) A major fraction of this particular type of soil is removed during the first minute of laundering, and that after 4 minutes the rate of removal is negligible.

g) In the laundering procedure used, the quantity of soil removed from all fabrics was nearly equal, but significantly greater residues of soil remained after laundering in those materials having initially high soil contents.

4) The principles and techniques described in the paper can provide a sound basis for practical and fundamental advances in the study of soiling and soil removal.

ACKNOWLEDGMENTS

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National Cotton Council of America
National Institute of Drycleaning
U S Department of Agriculture, Agricultural Research Service, Textiles and Clothing Section, Home Economics Research Branch

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TABLE V
SOILING AND DRYCLEANING OF ACETATE, RAYON, AND DACRON FABRICS

	Reflectance (R)			*Yellowness (b)*			*Soil Content*[a]	
Fabric	*Original Value*	*Decrease During Soiling*	*Decrease after Soiling and Dry Cleaning*	*Original Value*	*Increase During Soiling*	*Increase after Soiling and Dry Cleaning*	*Soiled*	*Cleaned*
Acetate	83.6	8.4	0.3	4.7	1.1	0.6	2.51	0.11
Rayon	83.1	6.8	0.3	2.7	1.2	0.9	1.83	0.05
Dacron	76.3	9.6	0.9	—0.7[b]	1.1	1.3	4.76	0.36

[a] The values given refer to calculated "soil content" as described in the text.
[b] Negative value of "b" indicates that the fabric is slightly blue.

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APPENDIX A

RATE OF SOILING STUDY—The general plan used in the rate of soiling study was as follows:

1) **Launder 5 collars of each fabric and measure reflectance.**
First laundering is for the purpose of removing finishing materials or soil accumulated during the making of the collars. When not in use, each collar was stored in a separate envelope or wrapped and handled with care to avoid extraneous soiling.

2) **Wear 4 collars of each fabric 2 hours and measure reflectance.**
The fifth collar for each fabric is used as a washing control and is not worn.

3) **Return collars to same test subjects, wear 3 hours and measure reflectance.**

4) **Return collars to same test subjects, wear 7 hours and measure reflectance.**

5) **Return collars to same test subjects, wear 7 hours and measure reflectance.**

6) **Return collars to same test subjects, wear 7 hours and measure reflectance.**
This gives a total period of wear of 26 hours.

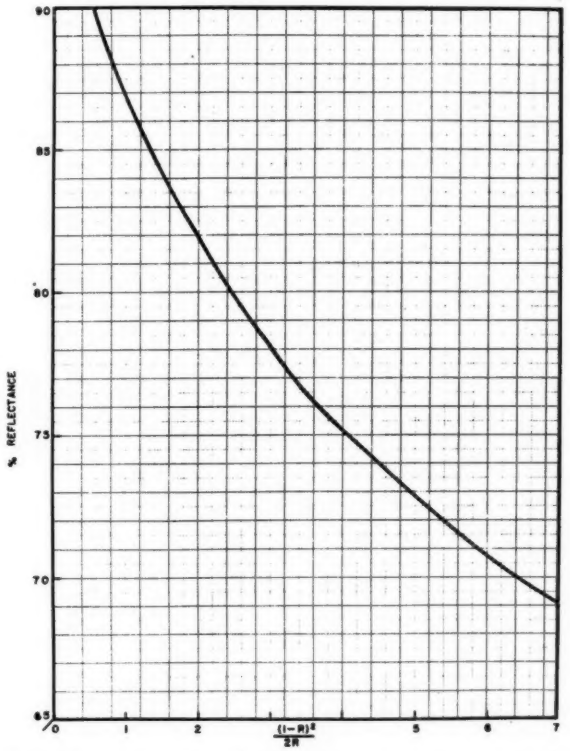
7) **Launder and measure reflectance of all samples, including washing control.**
In the case of the group of starched cotton broadcloth collars, an additional set of reflectance measurements were made after the collars were restarched and ironed.

Wearing Plan. **Four collars each, of 4 different type materials were used. These 16 collars could have been tested in a variety of ways. For example, 16 different subjects could be used, with each testing a different collar. However, this probably would not have been as good as having 4 test subjects each soiling one collar from each of the 4 different materials. The latter procedure, while eliminating the influence of test subject variability, is a more time consuming method. In these tests, therefore, a compromise method was adopted involving 8 subjects. These were personnel who did no traveling and were available 100% of the time except for illness or other emergency. The wearing plan used for the experiment on rate of soiling is typical of those employed throughout this study and is shown in the following table.**

Test Subj	*1st Day 2 hrs* (2 hrs 2 hrs) *	+	*2nd Day 3 hrs* (3 hrs 3 hrs)	+	*3rd 4th Day 7 hrs* (7 hrs 7 hrs)	+	*5th 6th Day 7 hrs* (7 hrs 7 hrs)	+	*7th 8th Day 7 hrs* (7 hrs 7 hrs)	= *Total 26 hrs*
1	A_1 B_1		Same plan as first day.		Same plan as first day.		Same plan as first day.		Same plan as first day.	
2	C_1 D_1									
3	B_4 A_2									
4	B_2 C_2									
5	D_2 C_4									
6	A_3 B_3									
7	C_3 D_3									
8	D_4 A_4									
	Make reflectance measurements after this wearing.		Make reflectance measurements after this wearing.		Make reflectance measurements after this wearing.		Make reflectance measurements after this wearing.		Make reflectance measurements after this wearing.	

* A, B, C, and D indicate type collar material—cotton, Dacron, etc. Subscripts denote the number of each of the 4 collars of the same material.

APPENDIX B



Conversion of R values of "soil content" using the formula $\frac{(1-R)^2}{2R}$

APPENDIX C

Wearing of the test collar

Pacific-Southwest Section——

WHITENESS RETENTION BY SATIN AND CREPE LINGERIE FABRICS DURING NORMAL WEAR AND CLEANING*

CLARICE H LINDSEY
Asst Professor of Home Economics
Univ of California at Los Angeles

Six college girls assisted in a co-operative work to evaluate nylon, rayon with acetate, and silk slips of crepe and satin weave, respectively, to determine how they compared in various properties for quality. The girls wore the slips and returned them to the lab where they were washed practically. For the lab study artificially soiled fabrics were attached to unsoiled swatches and laundered under similar conditions. The slips and samples were evaluated for whiteness retention by spectrol methods and for changes and in other physical properties by textile testing methods.

INTRODUCTION

STATEMENTS by students that lingerie made from nylon discolored to a greater degree than similar apparel made from other fibers focused attention on problems related to soiling and whiteness retention. Is discoloration due to fiber content, weave structure, or other factors? These were the questions that formed the framework for this laboratory and wear study.

Students taking courses in Home Economics at UCLA participated in a survey, which was an attempt to find out how they used and cared for the slips in their wardrobes. The information secured from the questionnaire was used in establishing the conditions for the study.

EXPERIMENTAL PROCEDURE

Slips and fabrics of nylon, silk, and a rayon-acetate blend were purchased from a nationally advertised manufacturer. Half, or eighteen of the slips and three of the fabrics, were crepe weave and the other half were satin weave. Six college girls participated in the wear study. Each girl wore three slips, a nylon, a silk, and a rayon-acetate, per week. The crepe slips were worn one week, then alternated with the satin slips while the former were being laundered and prepared for use again. Marking of the slips for the shrinkage and reflectance measurements was done by placing a ten-inch template on the fabric in the area of the diaphragm. Cross marks designated the midpoint and intersecting points of each of the four sides. The markings were made to run as nearly parallel to the warp and filling directions of the fabric as possible. Each slip had three pairs of markings in each direction, which were replaced by machine stitching so that the markings would last through use and repeated washings. The average of the three distances was considered as the measurement for the warp or filling. A Paragon Mechanical Draftsman Flat Scale divided into 1/100's of an inch was used for measuring. The placing and reading of the scale were facilitated by using a tripod lens. Fabric-thickness determinations were made with a Cady Automatic Hand Micrometer graduated in 1/1000's of an inch, and yarns were counted with a Lowinson Micrometer at the beginning and end of the study.

In the laboratory study, swatches approximately eighteen inches square were marked and measured, yarns were counted and thicknesses recorded in the same manner as was used for the slips. Bacon's *(1, 2)* method for the preparation of a standard soiled cloth was used for soiling the laboratory swatches. An unsoiled swatch of equal size and of the same weave structure was attached to each soiled swatch before laundering.

Approximately half of the students who answered the questionnaire used a washer for laundering their slips. Of this number 69.23 per cent used an automatic washer. Because of student usage and the greater availability of automatic washers in the Westwood area, an automatic home-type machine was used in this study.

The slips and laboratory fabrics were washed separately. The machine dial was set for the minimum washing time at the lowest temperature recommended for washing fine fabrics. The cycle took approximately 22 minutes, and the water temperature at the beginning of the washing period average 99.5° F. The water was softened with a phosphate-type softener. The ratio of softener and soap to the water was established in the laboratory. A neutral soap, one used by the largest number of students in the survey, was the detergent used for laundering. The slips and laboratory fabrics were partially dried in the automatic dryer, hand-ironed and kept over night on a horizontal surface before measuring. The slips and laboratory fabrics were measured for dimensional change after the first, fifth, and tenth washings.

A General Electric Spectrophotometer[1] *(9, 10, 11, 15)* was used to compare the light reflected from the fabric with the light reflected from the standard white magnesium carbonate, and the differences in reflectance were recorded as a graph across the spectrum. The slips were folded in thirds lengthwise and folded again crosswise just above the diaphragm area so that the reflectance measurement was taken in the marked area through twelve thicknesses of fabric. The laboratory swatches were equally folded, and an average of three readings was used. Samples were placed at 45°, which was in agreement with Judd, who stated "The angular conditions recommended for the colorimetry of opaque specimens are that the light shall strike the specimen at 45° and that the specimen shall be viewed along the perpendicular to its surface." *(6)* The coefficients of reflectance of magnesium carbonate *(3)* were used to correct the directional reflectance readings found for each fabric to perfect white. To determine the tristimulus value for Illuminant C the selected ordinate method *(4)* was used on the General Electric Tristimulus Integrator. The chromaticity coordinates were used in the Adam's formula *(5)* to compute color difference, and the size of the color difference was expressed in NBS (National Bureau of Standards) units, also called Judd's units. One NBS unit is a unit of color difference, which is five times the minimum perceptible color difference under the best viewing conditions. The NBS value range is

* Presented at the Gourmet Restaurant in Beverly Hills, Calif, on Friday, Mar 26, 1954. The ms was recd by the Editor of Proceedings on April 10 and by *Am Dyestuff Reptr* on Aug 16, 1954.

[1] We are indebted to Philip O'Brien of the College of Engineering of the Univ of California at Los Angeles for advice and suggestions for interpretation of the graphs.

Textile Terms	NBS (Judd) Units
trace	0.0- 0.5
slight	0.5- 1.5
noticeable	1.5- 3.0
appreciable	3.0- 6.0
much	6.0-12.0
very much	More than 12.0

Reflectance graphs were made for the slips and fabrics at the beginning of the study and after the fifth and tenth laundering.

The girls participating in the study kept a record of the hours each slip was worn. Observations regarding fabric characteristics were also recorded, and at the termination of the wear study each participant, using a rating scale, compared the slips she had worn.

Some statistical analysis has been used in this study along with visual analysis *(7)*. The deviation from type was shown by means of standard deviations, which were calculated for the mean reflectance values after wear and ten launderings. Fisher's "t" was used in testing the significance of the difference between means for unpaired variables. The hours of wear were correlated with the differences in reflectance.

EXPERIMENTAL RESULTS AND DISCUSSION

The crepe and satin fabrics used in the wear and laboratory study are described in Table I. Both the rayon crepe and the satin were acetate in the warp direction, the crepe had a viscose filling and the satin, a cuprammonium filling. All of the fabrics had more warp yarns per inch than filling yarns. Excepting the nylon crepe fabric, all laboratory fabrics were woven from yarns which had more twist in the filling direction. The fabrics used in the laboratory study were purchased as the same materials from which the slips had been made. The slips were lace-trimmed and of similar cut and construction with the exception of three rayon crepes, one of each size, which had tailored tops. Because of this difference a six-inch-square area was marked off for study on these slips instead of the ten-inch square which was used for the others. Thirty-six slips, six of each fabric and two each of sizes 12, 14, and 16, were worn by the students who participated in the study. Each slip was worn two days before laundering, but the hours per day the wearer was dressed, the activities, personal habits, and the kind, color and cleanness of the outer clothing worn were not controlled.

Table II shows the hours the slips were worn and the difference in reflectance after the second wear-launder cycle. The mean wear hours for the crepe slips was 232.0 hours and for the satins, 229.4 hours. The mean color difference, which is not statistically significant, was 6.49 NBS units for the crepe slips and 6.04 NBS units for the satins. When the wear hours and the color differences were correlated for all the slips by use of a 2×2 table, the $\times^2$ value was 5.36, showing a significant relationship. The "P" value for one degree of freedom at the 5-percent level is 3.814 and at the 2-percent level is 5.412.

The greatest mean loss and range in reflectance values was for the rayon satins. The original whiteness of the rayon crepe and satin was approximately the same. In the wear study, rayon (Figure 1) showed the greatest and the least color difference. The tendency toward yellowness was visually apparent in the new silk material, and the original reflectance values were less than the values for the rayon and nylon fabrics.

McKee and Roseberry *(8)* state that fibers of different chemical composition differ in the way they give up soil and that under the same washing conditions certain fibers clean more easily than others. In the wear study (Table III) there was no significant difference between the mean values for the fibers used. The laboratory results (Figure 2 and Table IV) indicate that the fabrics of satin weave used in this study released soil to a greater degree than the crepe fabrics.

This phenomenon seems to be associated with fabric structure rather than with fiber composition, since all the fibers studied are represented in each group. With the exception of the nylon satin (Table I), there was little difference in

TABLE I
PHYSICAL PROPERTIES OF THE NEW CREPE AND SATIN FABRICS

Property Measured	Unit of Measure	Rayon Crepe	Rayon Crepe	Silk Satin	Silk Satin	Nylon Crepe	Nylon Satin
Fabric count	no/inch						
Slip fabrics							
W		156.1	256.8	168.1	291.5	126.2	310.8
F		113.8	112.7	122.8	131.8	103.7	132.0
Lab fabrics							
W		154.4	257.6	159.0	288.8	128.2	315.8
F		112.0	111.6	117.8	129.8	102.2	134.6
Thickness	0.001 inch						
Slip fabrics		7.8	7.4	6.4	7.6	4.7	6.3
Lab fabrics		8.0	7.3	7.0	8.0	5.0	6.5
Wt per sq yd	ounces						
Slip fabrics		..	..	..	..	..	..
Lab fabrics		2.9	2.9	2.0	2.3	2.0	2.6
Yarn twist	no/inch						
Slip fabrics		..	..	..	..	..	..
Lab fabrics							
W		1.8	1.5	0.0	0.0	10.3	6.3
F		31.8	31.8	52.1	50.9	10.0	34.7
Yarn number	denier						
Slip fabrics		..	..	..	..	..	..
Lab fabrics							
W		75	50	55	35	45	45
F		75	75	50	50	45	45

TABLE II
WEAR HOURS AND REFLECTANCE VALUES IN NBS UNITS FOR THE CREPE AND SATIN SLIPS

		Crepes		Satins	
Fabric	Size*	Hours of Wear	Reflectance NBS Units	Hours of Wear	Reflectance NBS Units
Rayon & Acetate	12 a	193.00	3.00	193.00	4.85
	12 b	282.30	6.90	258.00	11.80
	14 a	195.00	6.00	185.00	12.50
	14 b	208.50	4.00	196.00	10.90
	16 a	294.00	3.50	289.00	19.10
	16 b	226.00	3.30	260.50	6.75
Silk					
	12 a	180.50	6.54	195.00	4.65
	12 b	281.80	11.25	287.00	8.00
	14 a	182.50	9.25	177.00	2.58
	14 b	205.50	9.34	200.00	2.24
	16 a	258.00	9.70	283.00	7.52
	16 b	228.00	6.20	241.00	6.70
Nylon					
	12 a	185.50	2.19	200.00	5.98
	12 b	284.50	9.04	239.50	6.19
	14 a	210.00	7.66	176.00	6.45
	14 b	208.00	5.29	202.50	1.43
	16 a	300.00	8.25	281.00	11.10
	16 b	253.00	5.38	265.00	7.66
Mean =		232.00	6.49	229.40	6.04
σ =			2.73		4.05
t = .24					

* Two girls of each size participated in the study
Value of "t" 17 degrees of freedom *(7)*
5-percent level, 2.110
1-percent level, 2.898

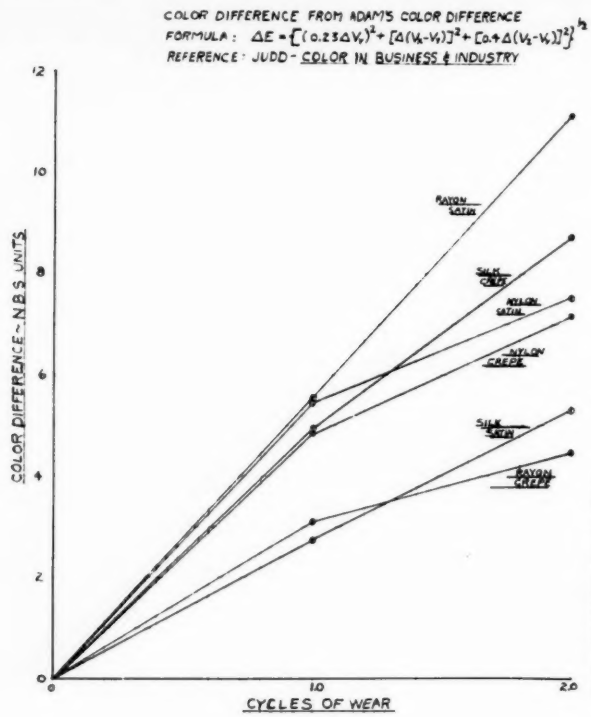

COLOR DIFFERENCE FROM ADAM'S COLOR DIFFERENCE
FORMULA: $\Delta E = \{(0.23\Delta V_1)^2 + [\Delta(V_4 - V_3)]^2 + [0.4\Delta(V_2 - V_1)]^2\}^{1/2}$
REFERENCE: JUDD - COLOR IN BUSINESS & INDUSTRY
COLOR DIFFERENCE - N.B.S. UNITS
RAYON SATIN
SILK CREPE
NYLON SATIN
NYLON CREPE
SILK SATIN
RAYON CREPE
CYCLES OF WEAR

Figure 1
Results of Slip Wear Test

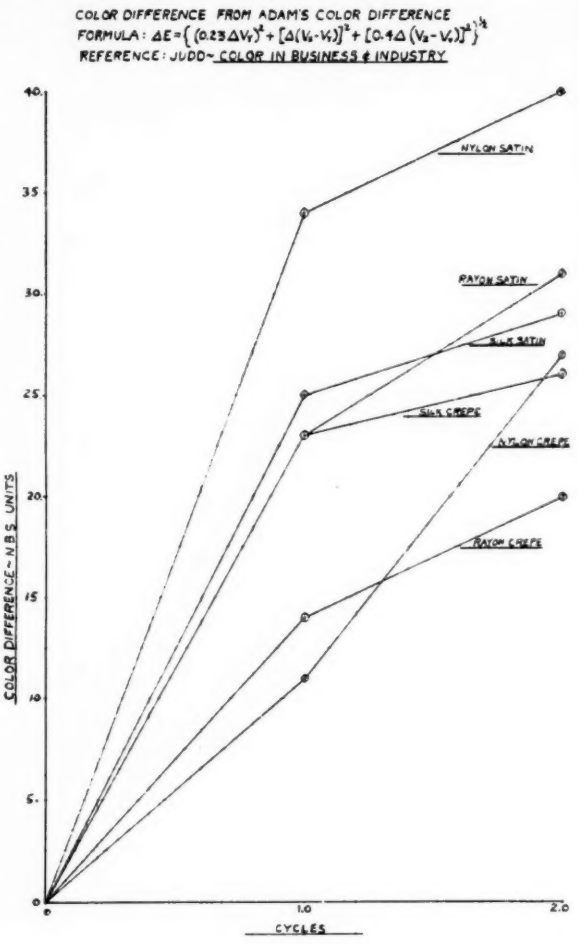

COLOR DIFFERENCE FROM ADAM'S COLOR DIFFERENCE
FORMULA: $\Delta E = \{(0.23\Delta V_1)^2 + [\Delta(V_4 - V_3)]^2 + [0.4\Delta(V_2 - V_1)]^2\}^{1/2}$
REFERENCE: JUDD - COLOR IN BUSINESS & INDUSTRY
COLOR DIFFERENCE - N.B.S. UNITS
NYLON SATIN
RAYON SATIN
SILK SATIN
SILK CREPE
NYLON CREPE
RAYON CREPE
CYCLES

Figure 2
Lab Results: Removal of Dirt from Soiled Fabric

the twist of the yarns used for the crepes and satins. Snell *(12)* found that a loosely woven fabric is easier to deterge than a tightly woven one. Satin, because of the floating yarns, would be less compactly woven than the crepes. The transfer of soil (Table IV and Figure 3) to the attached white fabric was greater in the silk than in the nylon or acetate rayon materials. Rayon crepe throughout the study changed the least. It remained more nearly white through wear. In the laboratory study, less soil was removed and the attached white swatch retained its whiteness to a greater degree. The nylon and rayon-acetate fabrics were similar in their whiteness retention. The mean loss in reflectance for the satins was 4.8 NBS units and for the crepes, 4.6 NBS units. In the soiled fabrics, the satins gained in reflectance after ten washings by 33.3 NBS units and the crepes, 24.3 NBS units.

When the loss in reflectance was ranked from the least to the greatest, there was no relationship between hours of wear, loss in reflectance and size of wearer. The participants seemed to fall into two groups (Table V). Each group was made up from one of each size. The same group relationship held for both the crepe and satin fabrics. The mean change in reflectance for the crepe slips for Group I was 5.03 NBS units and for Group II, 7.95 per cent. The mean wear hours were 209.67 and 254.22, respectively. Two participants in Group I had longer wear

TABLE III
MEAN WEAR HOURS AND COLOR DIFFERENCE IN NBS UNITS FOR THE CREPE AND SATIN SLIPS

	Hours	*Color Difference*
Rayon & Acetate	231.7	7.7
Silk	226.6	7.0
Nylon	233.7	6.4

TABLE IV
REFLECTANCE VALUES IN NBS UNITS FOR THE SOILED AND ATTACHED-WHITE FABRICS AFTER THE FIFTH AND TENTH WASHINGS

Fabric	*Color Difference Soiled Fabric*		*Color Difference White Fabric*	
	Cycle I	*Cycle II*	*Cycle I*	*Cycle II*
Rayon and acetate				
Crepe	14.0	20.0	2.0	3.2
Satin	23.0	31.0	2.6	3.8
Silk				
Crepe	23.0	26.0	5.3	7.1
Satin	25.0	29.0	5.4	7.1
Nylon				
Crepe	11.0	27.0	3.5	3.5
Satin	34.0	40.0	3.4	3.4

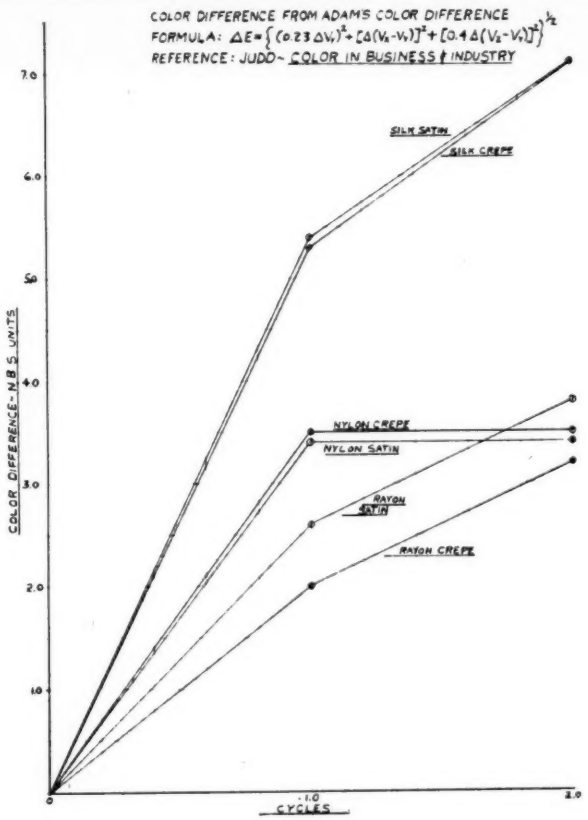


Figure 3
Lab Results: Transfer of Dirt to Clean Fabric

TABLE V

MEAN HOURS OF WEAR AND REFLECTANCE LOSS IN NBS UNITS FOR THE PARTICIPANTS IN THE WEAR STUDY

		Crepes		*Satins*	
		Loss in reflec	*Hrs worn*	*Loss in reflec*	*Hrs worn*
I	12a	3.91	186.30	5.16	196.00
	16b	4.96	235.70	7.03	255.50
	14b	6.21	207.30	4.86	199.50
Mean		5.03	209.67	5.68	217.00
	16a	7.15	284.30	12.57	284.33
II	14a	7.64	195.83	7.18	179.33
	12b	9.06	282.80	8.66	261.50
Mean		7.95	254.22	9.47	244.88

TABLE VI

MEAN PHYSICAL CHARACTERISTICS OF THE SLIP FABRICS BEFORE LAUNDERING AND AFTER WEAR AND TEN LAUNDERINGS

*Slips**	*Yarn Count Before Laundering* W	F	*Yarn Count After Laundering* W	F	*Thickness in 1/1000 in Before Laundering*	*Thickness in 1/1000 in After Laundering*	*Hours Worn*	*Shrinkage in Per Cent* W	F
Rayon Crepe	156.1	113.8	155.6	122.9	7.8	8.7	233.1	1.51	6.57
Rayon Satin	256.8	112.7	264.6	118.6	7.4	8.8	230.3	3.68	7.21
Silk Crepe	168.1	122.8	172.7	129.5	6.4	7.2	222.7	2.58	5.43
Silk Satin	291.5	131.8	298.9	138.2	7.6	9.4	230.5	4.62	5.44
Nylon Crepe	126.2	103.7	124.8	102.9	4.7	5.1	240.2	0.04	0.65
Nylon Satin	310.8	132.0	310.6	131.1	6.3	6.7	227.3	1.14†	0.35

* 6 slips in each group.

† Stretch.

hours than one of the participants in Group II. For the satin slips Group I had a mean loss in reflectance of 5.68 NBS units and Group II, 9.47 NBS units, and the mean wear hours were 217.00 and 244.88, respectively.

All of the slips shrank more in the filling direction than in the warp direction (Table VI). The nylon fabrics had slight dimensional change. Nylon satin gained in length. All of the slip fabrics increased in thickness after wear and laundering. Yarn count increased in both warp and filling for the silk and rayon fabrics, and for nylon there was a slight decrease.

The satin slips shrank more than the crepe slips. In the warp direction the mean shrinkage for crepes was 1.38 per cent and for satins 2.39 per cent. In the filling direction the mean shrinkage for crepes was 4.22 per cent and for satins, 4.33 per cent. Progressive shrinkage occurred in both directions and in all the fabrics excepting nylons, which showed good dimensional stability.

Each participant rated the slips she wore on a scale from one to three for superiority in the following properties: handle (feel), freedom from static electricity, freedom from body cling, conformability to body movement, strength of seams, flatness of seams (freedom from ripple), dimensional stability, and whiteness retention. As a result of these evaluations, the slips fell into the following order of quality from best to poorest: nylon crepe, nylon satin, rayon satin, rayon crepe, silk satin, and silk crepe.

SUMMARY

Six college girls in alternate weeks wore crepe and satin slips made from acetate-rayon, nylon and silk. Reflectance graphs were made on the slips at the beginning of the study and after the fifth and tenth wear period. For the laboratory study, similar fabrics were artificially soiled and, after being attached to unsoiled swatches, were laundered five and ten times and evaluated. In this study there was little difference in the loss in reflectance for fabrics of crepe or satin weave or between fabrics of different fiber content in both the wear study and the laboratory study of whiteness retention. In the laboratory study on soil removal from artificially soiled fabric, the satins released soil to a greater degree than the crepes. Weaver *(9)* found that soil removal ability varied little among the different makes of washers, but conventional washers had a slight advantage. She also found that the machine having a low set temperature gave the lowest degree of soil removal.

Washing-machine manufacturers recom-

(Concluded on page P770)

Piedmont Section——

IMPROVED WASH FASTNESS OF ACETATE-RAYON BLENDS*

V S SALVIN, A B CONCIATORI, R A WALKER, G C WARD and F FORTESS

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Dye-fixation processes were applied to acetate - rayon and acetate - rayon - nylon blends to give improved wash fastness of a level fast to machine washing at 120-130°F, with minimum shade change, and with marked reduction in staining. The shirting and slack fabrics retained satisfactory appearance and dimensions without significant attrition after 25-50 washes.

Principles underlying the fixation of acetate dyes by formaldehyde resins and copper fixatives are presented. The process makes use of selected, commercially available, acetate (disperse) dyes of high intrinsic wash fastness and fixation response in addition to fixable rayon dyes. Resins that can penetrate the acetate fibers show optimum results. The fixation takes place in a finishing treatment with urea-formaldehyde resins and copper fixatives applied by conventional procedures on regular finishing equipment.

I INTRODUCTION

IMPROVED wash fastness on acetate-rayon blends is of importance in view of the wide acceptance of such fabrics because of their styling potentiality, ease of dyeing, lower cost and desirable fabric properties *(1)*. With the increasing trend toward washability in slacks and shirtings, raising the level of wash fastness is of practical interest in order to give this blend improved balanced performance.

This problem has been attacked from the standpoint of a fixation process for commercially available acetate dyes using selected dyestuffs, copper fixatives and formaldehyde resins. This paper covers the principles established, their reduction to practice and description of the process as carried out in pilot plant and mill trials.

II PRESENT AVERAGE LEVEL OF WASHABILITY

Washability or launderability involves not only changes in color fastness, but also changes in fabric properties due to shrinkage and attrition. It is of no value to improve color fastness if the fabric shows excessive shrinkage or abrasion under conditions of home or commercial washing. In order to obtain data on general appearance, dimensional stability and weight change, 100% acetate, 50-50 acetate-rayon (resin-finished) and 100% rayon, both unfinished and resin-finished, were washed in synthetic detergent in an automatic home washer of the agitator type. The washing was carried out at 125°F. A full load was used, and up to 50 cycles of washing and intermittent ironing were employed.

The fabrics used were of spun yarn and of a construction suitable for such end uses as slacks or shirtings. Neither the acetate nor the resin-treated acetate-rayon showed any signs of severe physical degradation, such as tears or thin abraded sections. Photomicroscopic examination of the fiber bundles revealed no signs of fibrilation as compared with the unwashed fabric. The acetyl value of the acetate fiber was essentially unchanged. The shrinkage was 4-5%, and the weight loss was 5%. The data show that acetate and resin-treated acetate-rayon fabrics are washable in the broad sense, since they retained their original properties.

However, these fabrics, which had been dyed and finished by the usual procedures, showed pronounced color change after 5 washings at 125°F. The conventional procedures used for dyeing acetate-rayon blends give a ready explanation of the reason for the unsatisfactory level of wash fastness. The processes outlined in Table I represent procedures that are recognized by the practical dyer as those which have been used on the acetate-rayon blend.

This degree of wash fastness can be demonstrated as being due to the use of such intrinsically mediocre wash-fast colors as the prototypes of Celliton Blue BB, Amacel Red VIII, Interchem Blue B, Eastman Yellow GLF and Celliton Yellow G *(2)*. All of the commercial recipes for acetate-rayon fabrics which were made available contained at least one of the disperse dyes listed above. Unbalanced wash down results in both reduction in depth of shade and easily recognizable hue change.

The use of selected rayon dyestuffs that are improved in wash fastness by after-treatment with copper fixatives and resins is common practice for 100% rayon to obtain dyeings that are of high resistance to washing. These rayon dyestuffs were used in recipe #2 in Table I for the rayon fiber in the blend, whereas, the acetate fiber was dyed with dyestuffs of low intrinsic wash fastness. The fabric was then given the copper-fixative resin aftertreatment. The over-all wash fastness is still not good because of the failure of the acetate dye.

III INTRINSIC WASH FASTNESS OF ACETATE DYES

The first approach in raising the level

TABLE I
WASH FASTNESS FROM CONVENTIONAL DYEING PROCEDURES

Dyestuffs	*Finishes*	*AATCC Wash-Fastness Level*
Recipe #1—Tan Shade		
Pontamine Blue RLW Diphenyl Fast Red B Pontamine Yellow RW Interchem Blue B Celliton Pink BA Eastman Yellow GLF	Aerotex Cream 450 Catalyst AC	Both rayon and acetate dyeings fail #1 test (105°F). Severe wash down and staining.
Recipe #2—Tan Shade		
Cuprofix Blue GLN Cuprofix Yellow GL Cuprofix Rubine BLN Interchem Blue B Amacel Red VIII Eastman Yellow GLF	Aerotex Cream 450 Cuprofix 47 Catalyst AC	Rayon dyes fixed and pass #2 test, whereas acetate dyes fail #1 test. Heavy wash down and staining.

* Presented by V S Salvin at the Hotel Roanoke in Roanoke, Va, on Saturday, April 10, 1954. The ms was recd by the Editor of Proceedings on April 23 and by the Am Dyestuff Reptr on Aug 27, 1954.

TABLE II

EFFECT OF TEMPERATURE ON DYESTUFF LOSS AND DYEING BEHAVIOR

Dyestuff	*Dyeing Characteristic*	*% Color loss at 105°F*	*% Color loss at 120°F*	*% Color loss at 140°F*	*% Color loss at 160°F*
Interchem Yellow HDLF-40 1.8%	slow dyeing rate high temp required	4.4	7.7	13.0	21
Amacel Red 2B 1.5%	slow dyeing rate high temp required	5.2	9.0	16.9	20
Amacel Red Y 1.5%	slow dyeing rate high temp required	5.7	10.0	15.0	22.4
Interchem Rubine 3B 1.0%	slow dyeing rate high temp required	5.0	10.5	18.3	24.6
Celliton Blue AF 1.0%	slow dyeing rate high temp required	4.5	7.5	12.8	22
Eastman Yellow GLF 1.5%	rapid dyeing rate low temp required	18.9	28.9	40.5	63
Celliton Pink BA 1.0%	rapid dyeing rate low temp required	16.7	27.6	43.5	54

of wash fastness on acetate-rayon blends is the use of dyestuffs intrinsically high in wash fastness. The commercial range of acetate dyes contains a selected number of dyestuffs which possess improved wash fastness. These dyestuffs have not been widely recognized as possessing this property. It is particularly noteworthy that the yellows have been the most deficient in wash fastness. Interchem Yellow HDLF-40, Amacel Yellow CW and Artisil Yellow RCGFL have become available as dyestuffs of high intrinsic wash fastness and can be used to give a balanced range.

The intrinsic wash fastness of several acetate dyes has been measured as a function of washing temperature. The percent loss is based on spectrophotometric data on samples washed for 30 minutes in the presence of 5 g/l soap at a liquor ratio of 50:1. The wash fastness has been correlated with the dyeing rate of these dyestuffs.

The best intrinsic wash fastness is exhibited by dyestuffs which show slow dyeing rate and a dyeing rate which is appreciably raised at higher temperatures. The principle of "easy come, easy go" applies.

By careful selection of such dyestuffs of higher wash fastness as Eastman Blue GLF, Celliton Blue AF, Amacel Red 2B, Artisil Red C5BFL, Interchem Yellow HDLF-40, Amacel Yellow CW and Artisil Yellow RCGFW, it is possible, on 100% acetate, to obtain dyeings that easily pass the #1 AATCC wash test and, in most shades, that give excellent performance in the #2 AATCC test. If dyers and finishers had been using such dyestuffs in combination with the fixable direct colors for rayon, most of their fabrics would have given satisfactory wash fastness at the level of the #2 AATCC test. The following table gives a classification of intrinsic wash fastness for many dyestuffs in the acetate range. The A classification is for those showing best wash fastness.

TABLE III

CLASSIFICATION OF THE WASH-FASTNESS LEVEL OF DYESTUFFS

Dyestuff	*Foreign Prototype Number*	*Wash Fastness Classification*
Blues		
Eastman Blue GLF		A
Celanthrene Violet BGF		A
Celliton Blue Green BA	229	A
Amacel Violet Blue FSI		A
Interchem Blue 4RL	(227)	A
Celliton Blue AF	227	A
Interchem Blue B	228	B
Celliton Violet 6B	241	B
Celliton Blue BB	232	B
Celliton Navy Blue BA	(232)	B
Amacel Blue GLF and (AGF)		B
Celliton Fast Red Violet RN	237	B
Reds		
Amacel Red 2B		A
Amacel Red Y		A
Interchem Rubine 3B	239	A
Artisil Red C5BFL		A
Eastman Red GLF		B
Eastman Red 2BGLF		B
Amacel Orange BL	230	B
Celliton Fast Red GG	236	B
Interchem Acetate Bordeaux B	238	B
Celliton Fast Brown 5R	230	B
Celliton Pink BA	234	C
Celliton Pink FF3B	235	C
Amacel Red FSI		C
Amacel Red 6X		C
Celliton Pink RFA		C
Yellows and Oranges		
Amacel Yellow CW		A
Interchem Yellow HDLF-40		A
Artisil Yellow RCGFL		A
Eastman Yellow 2RGLF		B
Eastman Yellow GLF		C
Artisil Direct Orange R		C
Celanthrene Yellow GL		C
Celliton Yellow 4RL		C
Celliton Yellow 7G		C
Celliton Yellow G	242	C
Celliton Yellow 5G	245	C

IV FIXATION OF ACETATE DYES WITH RESINS AND COPPER COMPOUNDS

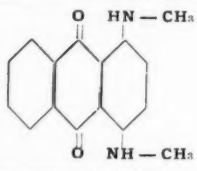
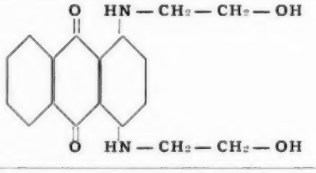
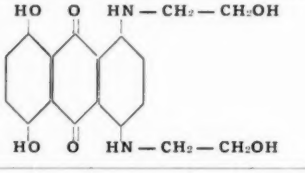
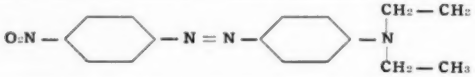
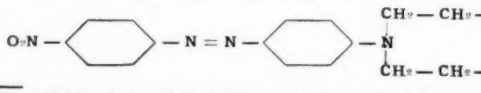
The wash fastness of acetate fabrics dyed with selected dyestuffs can be significantly improved by aftertreatment with formaldehyde-resin monomers and mixtures of these resins and copper fixatives. The principles of fixation of rayon dyes by means of cationic resins and by means of chelation through copper salts are well known *(3)*. The improvement in wet fastness of many rayon dyes by means of formaldehyde or ureaformaldehyde is also known *(4)*. However, the possibility of increasing the wash fastness of acetate dyes by resin or copper fixatives has received but little attention.

When dyed fabrics are aftertreated with formaldehyde resins alone, practically all dyestuffs show some degree of wash fastness improvement, but a select number show a much greater increase. When certain dyes are used with combinations of resin and copper fixative, there is additional improvement beyond that shown from resin alone. Since resin aftertreatment has been shown to effect complete insolubility of the acetate fiber in acetone, these experimental observations suggest the following three mechanisms as involved in the improvement of the wash fastness of the dyestuffs:

1) Interaction of the formaldehyde resin with the various reactive groups of the dyestuffs.
2) Interaction of the copper derivative with a chelatable group on the dyestuff.
3) Reduction of the outward diffusion of the dyestuff through change in the physical nature of the fiber, i e, hot-wet swelling characteristics or formation of an impermeable surface barrier.

The relative importance of the three mechanisms can be shown by examination of the fixation on various structures. The dyestuffs were especially synthesized to insure purity. The dyed fabrics were padded (a) with 5% urea-formaldehyde resin Rhonite R-1 and (b) with a combination of 5% Rhonite R-1 and copper fixative

TABLE IV
RELATIONSHIP OF DYESTUFF STRUCTURE TO AFTERTREATMENT SHADE CHANGE AFTER #3 AATCC WASH

DYESTUFF	FINAL RATING FOR RESISTANCE TO SHADE CHANGE: ORIGINAL	PADDED WITH RECIPE #1 — RESIN	PADDED WITH RECIPE #2 — RESIN + COPPER
1) 	2	2+	2+
2) 	2	3-4	3-4
3) 	2	3-4	4-5
4) 	2	2+	2+
5) 	2	3-4	3-4

Key to Table: Rating of Shade Change by International Grey Scale
1) very heavy color loss 2) heavy color loss 3) moderate color loss 4) slight color loss 5) practically no color loss

Cuprofix 47. The structures and results are given in Table IV.

Dyestuffs #1 and #4 in Table IV show very little improvement in wash fastness after treatment with either UF resin or combinations of UF resin and copper. These are dyestuffs which do not contain reactive amino or hydroxyl groups and which therefore do not react with urea-formaldehyde resin. The improvement observed is due to a change in the physical nature of the fiber (mechanism #3).

Dyestuffs #2 and #5 contain reactive hydroxy groups. They show a pronounced increase in wash fastness due to interaction of these reactive groups with the urea-formaldehyde resin. The mechanism of this reaction is the formation of a methylene bridge between the alkyl-hydroxy groups and the methylol groups of the formaldehyde resin. In Table V it is seen that other reactive groups may be present on acetate dye structures which will form methylenic bridges to give larger molecules of reduced diffusion rate.

A comparison of dyestuffs #2 and #3 shows an additional improvement in wash fastness due to addition of copper fixative to the resin pad bath. The two phenolic hydroxy groups on the anthraquinone ring of dyestuff #3 are chelating groups, which are capable of reacting with metallic ions such as copper to form metalized complexes.

On the basis of these mechanisms, a representative range of acetate dyes of known structure were evaluated as to their fixation response to formaldehyde resins and to copper compounds. The results are tabulated in Table V.

On the basis of these data, it is possible to select dyestuffs (a) of good fixation

TABLE V
RELATIONSHIP OF COMMERCIAL DYESTUFF TO FIXATION BY RESINS AND COPPER

Dyestuff	Chelatable Group	Resin Fixable Group	Response to Resin	Response to Cupric ion	Improvement in Wash Fastness with Cuprofix-Resin Bath
Celliton Blue Green BA	2 — OH*	2 — R — OH**	++***	+	From #1 to #3 AATCC test
Eastman Blue GLF	2 — OH	2 — OH 1 — R — OH	++	+	From #2 to #3
Interchem Blue B	none	none	—	—	Remains at #1+
Celliton Blue BB	4 — NH_2	4 — NH_2	+	+	From <#1 to #2
Amacel Red 2B	none	2 — ROH	++	—	Best of reds-improved with resin only, passes #2 test
Amacel Red Y	none	2 — ROH	++	—	Improved with resin, passes #2 test
Interchem Rubine 3B	none	2 — ROH	++	—	Improved with resin, passes #2 test
Eastone Red GLF	none	1 — ROH	+	—	Improved with resin, passes #2 test
Celliton Pink BA	1 — NH_2 1 — OH	1 — NH_2 1 — OH	++	+ (marked shade change)	From <1 to 2+ with marked color change
Celliton Pink RFA	1 — NH_2 1 — OH	1 — NH_2 1 — OH	++	+ (marked shade change)	From 1 to 2+ with marked color change
Amacel Orange BL	none	2 — ROH	++	—	Improved with resin to #2
Celliton Orange Brown 3RA	none	1 — R — OH	+	—	Improved with resin to #2
Amacel Yellow GLF	none	SO_2NH_2	—	—	No improvement
Amacel Yellow CW	none	NH — Aryl	+	—	Slight improvement with resin, passes #2
Interchem Acetate Yellow HDLF-40	none	NH — Aryl	+	—	Slight improvement with resin
Amacel Orange R	none	1 — NH_2	+	—	Slight improvement with resin

* OH represents phenolic hydroxy
** R — OH represents aliphatic hydroxy
***++ = marked improvement
+ = slight improvement
— = no improvement

response to resins, (b) of additional fixation response to copper, (c) of minimum shade change and (d) of optimum wash fastness behavior through combination of high intrinsic wash fastness and improvement through fixation. The range contains such dyestuffs as Celliton Blue Green BA or Eastman Blue GLF, which combine high intrinsic wash fastness, fixation by copper compounds and fixation by resins. In the reds, the high intrinsic wash fastness characteristic of Artisil Red 5RGLF and Amacel Red Y is further improved by resin fixation. Among the yellows are dyes of high intrinsic wash fastness, such as Interchemical Yellow HDLF-40. These yellows give an intermediate fixation response.

V VARIABLES OF RESIN TYPE AND APPLICATION CONDITIONS INFLUENCING WASH-FASTNESS LEVEL

The following variables are of importance in obtaining the optimum level of wash fastness with any particular dyestuff:

1) Resin type
2) Amount of resin
3) Catalyst
4) Copper fixative

Generally, the more resin applied the greater the improvement in wash fastness. A quantity of 5% on 100% acetate gives significant improvement. Further increase in resin application gives additional improvement up to 10%.

There are significant differences in the effectiveness of fixation by various resins. The best structures for effective fixation are those with small, stable molecules having a high ratio of formaldehyde to urea or melamine and preferably the presence of methoxy groups on the methylol unit. The most effective structures are the more stable ethylene-urea derivatives, including those which are methoxylated. This type of monomer, because of its structure, does not readily react with itself and consequently reacts with the dyestuff or the substratum. The presence of the methoxy groups also increases the penetration within the acetate, hence the resin and dyestuff are in better position to interact when polymerization occurs on curing. The effectiveness of the resins on application to acetate-rayon blends is not so effective as on 100%-acetate fabrics. The use of resin that favors penetration of acetate is even more important in the acetate-rayon blend because of the tendency of the rayon to adsorb the resin selectively. The effectiveness of a resin can also be correlated to the degree of acetone insolubility.

The resins, as represented by Aerotex Cream 450 and Rhonite 610, show significant fixation tendency. However, improved fixation is obtained in the following ascending order: Finish EN, Aerotex 802, Rhonite R-2, Aerotex 801, Rhonite R-1 and Aerotex M-3.

A EFFECT OF CATALYST———Examination of a number of catalysts with various resin monomers showed that some were more effective than others. In particular, oxalic acid and Accelerator UTX gave the least improvement in wash fastness. This may be due to their low penetration rate into the acetate. Catalyst G-8 and Catalyst A gave best results over the range of resins, Catalyst AS and Accelerator 187 giving slightly less effective results. Catalysts were effective in minimum concentration of 5% on weight of resin, but it is advisable to use a concentration somewhat above 5%.

B EFFECT OF COPPER FIXATIVES ———It was noted that not all commercially offered copper fixatives gave good results in the fixation process. Those with a minimum of copper have given the best results. It is advisable to determine, by preliminary trial, whether the copper fixative interferes with the fixation of the acetate dyes. Cuprofix 47 has given good results and can be used as a standard.

Further work remains to be done on the best combination of resin, catalyst and copper fixative to get optimum results. Of theoretical and practical interest are the findings that (a) addition of excess formaldehyde to the UF resin raised the fixation degree of the acetate dye, (b) presence of free copper salts reduced fixation, and (c) presence of materials such as urea (used for odor prevention) markedly reduced fixation.

VI APPLICATION OF FIXATION TREATMENTS TO ACETATE AND ACETATE-RAYON BLENDS

The principles of fixation of selected acetate dyes by urea-formaldehyde resins and copper fixatives have been applied in a series of laboratory and plant trials to 100% acetate. The dyestuffs used were from the recommended range which combine Class A intrinsic wash fastness and fixation response. The formulation used was as follows:

5% Rhonite R-1
1% Catalyst G-8
2% Cuprofix 47
Cured at 160°F for 5 minutes.
Light afterscour.

The wash fastness level is summarized in Table VI. It will be noted that the fabrics show excellent resistance to washing at 120°F. Performance was good at the 140°F washing temperature with shade change and staining becoming only clearly noticeable with the #3 AATCC test (160°F).

Light fastness and gas-fading resistance are not affected by resin treatment of the dyed acetate fabrics.

APPLICATION TO ACETATE-RAYON BLENDS ——— The resin-fixation process applied to acetate-rayon blends, in which the rayon is dyed with "cuprofixable" colors and the acetate is dyed with colors that respond to fixation, has made it possible to raise the wash fastness level of acetate-rayon slack and shirting fabrics to better than the #2-wash-test level. This represents a marked improvement over most of the present commercially available acetate-rayon fabrics, which do not pass the #1 AATCC test for shade change and staining. The process used combined the best practices employed for fixation, by copper fixatives, of selected rayon dyes on rayon with the use of fixable acetate dyes and resins that penetrate acetate rather than with the conventional urea-formaldehyde type.

The acetate-rayon fabric (8.5-oz, 2/2 twill, 50-50 acetate-rayon slack fabric) was dyed to union shades with combinations of "cuprofixable" dyes and selected acetate dyes, which were the same ones that were used for 100% acetate. The dyeing procedures were essentially the same as for the conventional acetate-rayon.

In application on 50-50 acetate-rayon blends the rayon dyestuffs used were selected for maximum fixation possible by copper fixatives aided by the resin. These dyestuffs are well known to the dyer. For a series of laboratory and plant trials, the fixable dyestuffs for the rayon were as follows:

Cuprofix Blue GLN and Blue LUL
Cuprofix Rubine BLN
Cuprofix Yellow GL;

and for the acetate, the following:

Eastman Blue GLF
Celliton Blue AF
Amacel Red 2B
Interchem Yellow HDLF-40
Amacel Orange BL

For the best results on acetate, the urea-formaldehyde resins of the acetate penetrating type, such as Aerotex 801 and Rhonite R-1, are recommended. However, since these resins do not give optimum effects for hand and resilience on a rayon blend, resin combinations should be used that include those best suited to the rayon.

VARIATION IN EFFECTIVENESS OF DYESTUFF FIXATION WITH RESIN STRUCTURE

	Fixation of Amacel Red 2B
Low ratio of formaldehyde to urea	least
High ratio of formaldehyde to urea	intermediate
Methylated high ratio of formaldehyde to urea-dimer	intermediate
High ratio of formaldehyde to alkylated urea	maximum

TABLE VI

WASH FASTNESS ON 100% ACETATE AFTER FIXATION TREATMENT

Shade	Dyestuffs	#2 Test (120°F) SC*	#2 Test (120°F) St*	#2½ Test (140°F) SC	#2½ Test (140°F) St	#3 Test (160°F) SC	#3 Test (160°F) St
Green	Eastman Blue GLF, I/C Yellow HDLF-40	4-5	5	4	4	3-4	3
Brown	Eastman Blue GLF Amacel Red 2B I/C Yellow HDLF-40	4-5	4	4	3-4	3-4	3
Red	Amacel Red 2B	4-5	5	4	4	3-4	3
Navy	Celliton Blue Green BA Amacel Red 2B I/C Yellow HDLF-40	5	4	4-5	4	4	3

* SC = Shade Change
* St = Staining

Cost considerations also contribute to resin choice. The resins used included Finish EN, Rhonite R-1, Aerotex 801 and Rhonite 610.

The resins were applied at 10-12% solids on the fabric. Cuprofix 47, 2% on pad-bath volume, has been generally used. Other copper fixatives should be screened to determine whether they interfere with fixation of the acetate dyes, as several commercially available copper fixatives have been shown to interfere.

The relative effectiveness of the urea-formaldehydes of varying structure for fixation shown for 100% acetate is also of the same relative order on acetate-rayon fabrics. As established on 100% acetate, optimum catalysts and copper fixatives are recommended. The shade change observed with some acetate dyes introduces no new problem over that noted in the fixation process for 100% viscose. Curing conditions are the same as those in general use for rayon and rayon blends, i e, 302-320°F (150-160°C) for 5 minutes. A light rinse after curing is used.

The resin-fixation process described above, when applied to the acetate-rayon blend, gives good fixation for the rayon dyes equivalent to that on 100% rayon. However, the fixation of acetate dyes is lower on an acetate-rayon blend than on 100% acetate. In padding 100% acetate there is no competition for the resin. In the acetate-rayon blend the resin is disproportionately absorbed by the rayon, thereby reducing the resin available for fixation within the acetate fiber. The quantitative differences in degree of fixation have been determined by spectrophotometric determinations of the dye in the wash liquor. The values are in the absence of the copper fixatives and on fabrics in which only the acetate fiber is dyed. These values, when combined with the intrinsic wash fastness of the dyes listed in Table I, give a quantitative picture of the percentage dyestuff loss under various washing conditions. In the case of the blues additional fixation is obtained by the use of Cuprofix. The best wash fastness is obtained by the use of a dyestuff of intrinsically high wash fastness in combination with the most effective fixatives.

APPLICATION TO ACETATE-RAYON-NYLON BLENDS——The fixation process applied to acetate-rayon-nylon blends gave wash fastness results that were equivalent to those obtained on acetate-rayon blends.

The decrease in abrasion resistance on acetate-rayon blends due to resin applications makes it desirable to add nylon to the blend in order to compensate for the decrease. A 45-40-15 acetate-rayon-nylon blend was chosen to show the effect of nylon addition.

The application of Rhonite R-1 resin to 100% nylon under the same conditions as used for 100% acetate showed that dyestuff fixation occurs also on this fiber.

The entire range of dyestuffs used for fixation on acetate cannot be used for union-dyeing acetate-nylon blends. The Eastman Blue GLF and Amacel Red 2B will union-dye both fibers, but the recommended yellows do not, since these have low affinity for the nylon. In tertiary shades, such as browns, the acetate fiber dyes brown, whereas the nylon is violet. The solution to this problem lies in the use of a yellow selected from the Irgalans, Cibalans, Capracyls, or Supralans. They have affinity for nylon but do not dye the acetate. The addition of the yellow dyestuff, Irgalan Yellow 2RL, to the dyebath resulted in union dyeing.

The finishing recipes used for the 45-40-15 acetate-rayon-nylon blend parallel those used for the acetate-rayon blend. The wash fastness results are equivalent to those obtained on the same shade of acetate-rayon.

TABLE VII

FIXATION OF COMMERCIAL DYES ON SPUN SLACK FABRICS

Dyestuff, 2% Dispersed Powder	% Improvement with 10% Rhonite R-1 and Catalyst G-8: Acetate	% Improvement with 10% Rhonite R-1 and Catalyst G-8: Acetate-Viscose
Amacel Yellow CW	56	24
Amacel Orange BL	83	70
Amacel Red 2B	86	65
Celliton Blue Green BA	85	68
Eastman Blue GLF	84	72

FORMULATIONS USED IN MILL TRIALS FOR THE DYEING AND RESIN TREATMENT OF ACETATE-RAYON BLENDS

Dyestuff

Navy
Celliton Blue AF
Amacel Red 2B
Interchem Yellow HDLF-40
Cuprofix Blue LUL
Cuprofix Rubine BLN
Cuprofix Yellow GL

Grey
Eastman Blue GLF
Amacel Yellow CW
Artisil Red 5BGLF
Cuprofix Yellow GL
Cuprofix Rubine BLN
Cuprofix Blue GL

Brown
Eastman Blue GLF
Amacel Orange BL
Amacel Red 2B
Cuprofix Yellow GL
Cuprofix Rubine BLN
Cuprofix Blue GL

Pad Bath

10% Aerotex 801
6% Rhonite R-1
3% Cuprofix 47
1.5% Catalyst G-8
1.25% Softener H

7.5% Finish EN
5% Rhonite R-1
2% Cuprofix
1% Catalyst G-8
1.25% Softener H

WASH FASTNESS —— The wash fastness level obtained by these procedures can be expressed in terms of a) behavior under the accelerated AATCC tests for washing at 120°F (#2 test) and 160°F (#3 test) and also at 140°F, b) the behavior on repetitive washing in home washing machines at 130°F and 140°F, and c) the behavior under repetitive commercial laundering conditions at 130°F. A summary of the washing tests is in Table VIII.

The results of Table VIII show that

1) Under accelerated washing conditions fabrics pass the #2 test regardless of shade.
2) They are borderline with respect to shade change and staining at 140°F.
3) Shade change and staining, especially in heavier depths, are evident at the 160°F test.
4) The over-all wash fastness is markedly superior to that of acetate-rayon dyed in the conventional manner.

Under home machine washing, five repetitive washings at 130°F are required to give a readily detectable shade change. The shade change is less pronounced and more on tone than that on the washed fabric given a single #3 AATCC wash test. Five repetitive washes in a commercial washing machine at 130°F gives slightly greater wash down than that of the home washer.

TABLE VIII
WASH FAST LEVEL ON ACETATE-RAYON

	120°F		140°F		160°F		5 repeated machine washings at 130°F
	SC*	St*	SC	St	SC	St	SC
Navy	4-5	slight	4	mod*	3-4	mod	4
Grey	4-5	none	3-4	sli*	3	mod	3-4
Brown	4-5	none	4	sli	3-4	mod	3-4

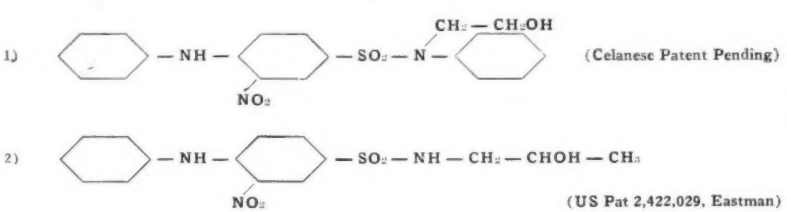
* SC = Shade Change
* St = Staining
* mod = moderate
* sli = slight

The principles and the data discussed in this paper permit the achievement of a range of wash fastness levels through a choice of dyestuffs and of resins with respect to type and quantity. The fabric-end-use requirements and the dyeing and finishing procedures will be determining factors. As for dyestuff cost, the selected dyes will not be significantly higher in cost for yellows and reds. The blues of good intrinsic wash fastness and fixation response are higher in cost. Copper fixatives represent a constant cost factor since they are also used for the rayon dyes.

The typical urea-formaldehyde cross-linking resins of the low-ratio-of-formaldehyde-to-urea type when used with fixable dyes provide a significant level of fixation. This is sufficient to achieve the #2-AATCC-wash fastness level for shade change and for staining in all but the heavy shades. The use of modified urea- or melamine-formaldehyde resins of the acetate penetrating type gives a more effective dyestuff fixation. The wash fastness is raised to the level of satisfactory shade retention in the home laundry and a 20°F improvement above the #2 AATCC test. Although the modified resins may be more expensive than the standard type, their use is indicated where optimum wash fastness is desired.

The wash down observed is most noticeable in the Amacel Yellow CW component. Reference to Tables II, III and VII shows that the yellow dyestuff, though of high intrinsic wash fastness, is not fixed to as high a percentage as the red and blue. Experimental yellows have been synthesized in the Celanese laboratory which possess the desirable high wash fastness and which give good fixation response. The following two structures utilize the principle of the reactive alkanol group, which responds to fixation.

The dyestuffs are in the diphenyl amine series and possess good light and gas-fading resistance and are not phototropic.



Pruf, etc, and stearyl-melamine derivatives have been employed in conjunction with the urea-formaldehyde resins to impart durable water repellency, spot resistance, sewability, and glazing resistance, as well as to overcome deficiencies in abrasion resistance and tear strength.

The injurious effect on flex abrasion and on tear strength of most urea-formaldehyde resins is illustrated in Table IX.

TABLE IX
EFFECT OF RESIN TREATMENT ON ABRASION AND TEAR STRENGTH

Resin Type		Flex Abrasion Dry Warp	Flex Abrasion Dry Fill	Flex Abrasion Wet Warp	Flex Abrasion Wet Fill	Dry Tongue Tear Warp	Dry Tongue Tear Filling
100% Acetate Suiting							
Original Unfinished		76	62	48	46	3.5	3.5
Resin 610	3%	53	48	37	28	3.0	3.0
Resin 610	3%						
Permel	1.5%	102	85	58	42	5.4	5.9
Rhonite R-1	3%	49	57	39	30	3.2	3.5
Rhonite R-1	3%						
Permel	1.5%	135	119	56	52	6.8	6.8
50-50 Acetate-Rayon							
Original Unfinished		286	139	94	84	4.3	4.3
Resin 802	10%	154	165	127	108	5.9	6.8
Resin 802	10%						
Permel	1.5%	99	175	106	90	8.4	8.5
Acetate-Rayon-Nylon, 45-40-15							
Original Unfinished		10,562		825			
Rhonite R-1	5%						
Cream 450	12.5%	206		513			
Rhonite R-1	5%						
Cream 450	12.5%	9,817		952			
Decetex 104	3.4%						

VII EFFECT OF RESIN TREATMENT UPON FABRIC MECHANICAL PROPERTIES

The general experience of the textile industry is that the application of the melamine- and urea-formaldehyde resins to rayon-containing fabrics results in decreased abrasion resistance and tear strength. Since these resin treatments are essential for the improvement of the shrinkage and resilience of the rayon portion, some means must be found to overcome these undesirable effects of reactive resins. Wax-type cationic softeners or surface lubricants have been generally employed in conjunction with these resins to improve the hand by decreasing stiffness while enhancing such secondary properties as sewability.

The use of 10-20% nylon in the blend has been found to raise the abrasion resistance of the fabric sufficiently that the loss due to resin treatment still leaves a fabric with satisfactory performance characteristics .

More recently, finishes based on the silicones, such as Decetex 102, 104, Hydro-

In general, the use of Permel or a silicone in combination with a urea-formaldehyde resin improves tear strength and reduces the detrimental effect on abrasion resistance.

Durable water repellency is also imparted by the use of silicones or Permel. In addition, these combination resin treatments give improved resistance to Hoffman Pressing and an increase in safe ironing temperature. Permel also improves gas-fading resistance because of its melamine content. Whenever possible, the use of silicone and Permel should be recommended to attain these added performance characteristics.

SUMMARY AND CONCLUSIONS

Based on data obtained from the repetitive machine washing of shirting and slack fabrics, acetate and acetate-rayon blends are shown to retain satisfactory appearance and dimensions without significant attrition after 25-50 washes. Principles underlying the fixation of acetate dyes by formaldehyde resins and copper fixatives have been established. Acetate dyes containing amine or aliphatic-hydroxy groups interact with the methylol group of the formaldehyde resins. The copper fixatives act by complex formation

through interaction of the copper ions with the chelatable groups when present in the anthraquinone-dyestuff structure.

A fixation process is described, which can be used on acetate-rayon or on acetate-rayon-nylon blends to give improved wash fastness of a level fast to repetitive machine washing at 120-130°F. The process uses selected acetate dyes that combine high intrinsic wash fastness and fixation response. The fixation takes place in a finishing treatment with urea-formaldehyde resins and copper fixatives by conventional finishing procedures on commercial equipment.

Variables for a particular dyestuff affecting the percent fixation and therefore the corresponding level of wash fastness have been isolated as follows: a) resin type, b) resin concentration, c) catalyst, and d) copper-fixative type. Areas of further work for new dyestuffs and more effective resins are indicated.

ACKNOWLEDGMENTS

We wish to acknowledge the assistance of the Sandoz Chemical Company in the selection of dyestuffs and of the American Cyanamid Company and Rohm and Haas Company for providing new and special cross-linking resins.

Reiner Stoll directed the research project and Sheldon Sprague and Harold F Elsom obtained the data on the effect of repeated washing on the mechanical properties of the fabrics. Appreciation must be expressed to the Celanese Corporation of America for encouraging the investigation and for granting permission for publication of the principles and data presented.

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Whiteness Retention——

(Concluded from page P763)

mend low temperatures and short wash periods for laundering fine fabrics, but further study is necessary to determine the optimum temperature, detergent type and concentration and wash period for most efficient detergency and least change in fabric properties. A more extensive study might reveal that differences in soil removal and whiteness retention between fibers and fabrics are more closely related to personal habits, dye and soil transfer from outer clothing, or static and soil particle size than to fiber content and weave structure.

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Membership Applications——

(Concluded from page P750)

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• Althouse Chemical Co, Inc Sold to Crompton & Knowles

The oldest independent dyestuff and intermediate manufacturing company in the United States, the Althouse Chemical Co, Inc, has become a wholly owned subsidiary of Crompton & Knowles Loom Works, which is reputedly the world's largest producer of fancy weaving equipment.

In a recent interview at the Althouse plant in Reading, Pa, with C Scott Althouse, president of Althouse Chemical, and William W Anthony, Jr, manager of commercial development of Crompton & Knowles, it was confirmed that no change in personnel, plant location or operating policies of the Althouse Company is contemplated. Dr Althouse will continue as president and a director and will direct the Company's activities as he has done since he and his late father, Nathan Althouse, founded it in 1915.

To further clarify the intention of Crompton & Knowles, the following letter is being sent to the trade:

"To our friends in the textile industry:

"It was with a great deal of satisfaction and assurance of continued success of both companies that we recently announced the purchase of Althouse Chemical Company, Inc by Crompton & Knowles Loom Works.

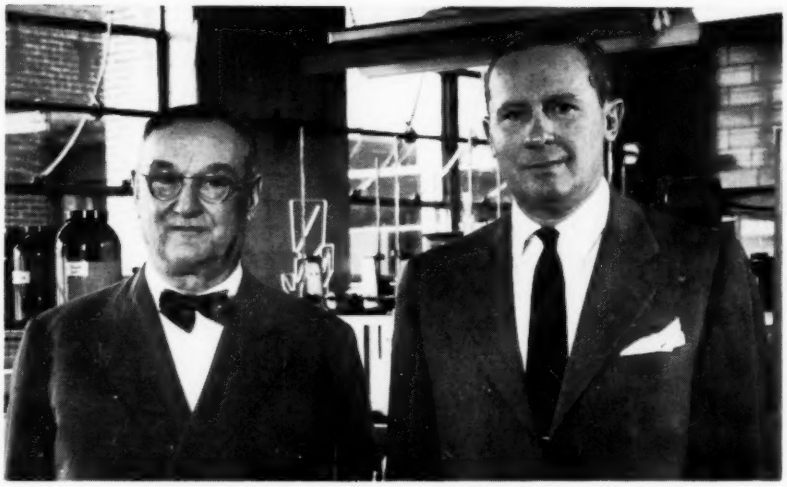
"Althouse dyestuffs and allied chemicals, like our weaving machinery, have earned a reputation for quality over the years, and each of the companies is recognized for its prompt and competent technical service available to the textile industry.

"The Althouse company, guided by Dr Althouse and his personnel, will continue to serve the textile industry by providing the highest quality dyestuffs and allied chemicals, offering the same efficient technical service, and assisting in any possible way in the production of quality fabrics. New laboratory developments are in process which we feel will enable us to be of even more service to the dyeing and finishing field.

"We look forward to a continuing fine relationship with all of those companies in the textile industry that are in a position to take advantage of our products and services.

"Cordially yours,
"FREDERIC W HOWE, Jr
President and General Manager, Crompton & Knowles Loom Works
Chairman of the Board, Althouse Chemical Company, Inc
"C SCOTT ALTHOUSE
President, Althouse Chemical Company, Inc"

Frederic W Howe, Jr, president of Crompton & Knowles, and Mr Anthony have become directors of the Althouse Chemical Company, Inc.



C Scott Althouse, left, and Frederic W Howe, Jr

It is felt that the combined technical knowledge of C & K in the building of textile weaving machines and the experience of Althouse Company in the wet-processing phase will enable both companies to broaden their service to the whole textile industry.

Entering into the dyestuff and intermediate manufacturing field marks the initial step in the plans of Mr Howe and his company to broaden their activities not only in this related phase of the textile industry but also, at a later date, in other industrial fields.

NOTICE

The Synthetic Organic Chemical Manufacturers Association will supply filing cards and instructions for filing data with the U S Customs in accordance with treasury decision 53594. The offices of SOCMA are located at 41 East 42nd Street, New York 17, N Y.

The purpose of T D 53594 is to establish a central reference file of samples of coal tar products produced by domestic manufacturers, together with accompanying technical data, to enable customs officers to compare each imported coal tar product with any comparable domestic product in order to ascertain its competitive tariff status.

Filing cards should be filed in duplicate with the Chief Chemist, U S Customs Laboratory, 201 Varick Street, New York 14, N Y, together with samples and color card data.

Producers of dyestuffs have indicated that they plan to give full support to this request for information. Information furnished U S Customs is held confidential in accordance with law. The regulation becomes effective December 22, 1954.

• Aula Continues to Broaden Line with New 3000 Series Colors

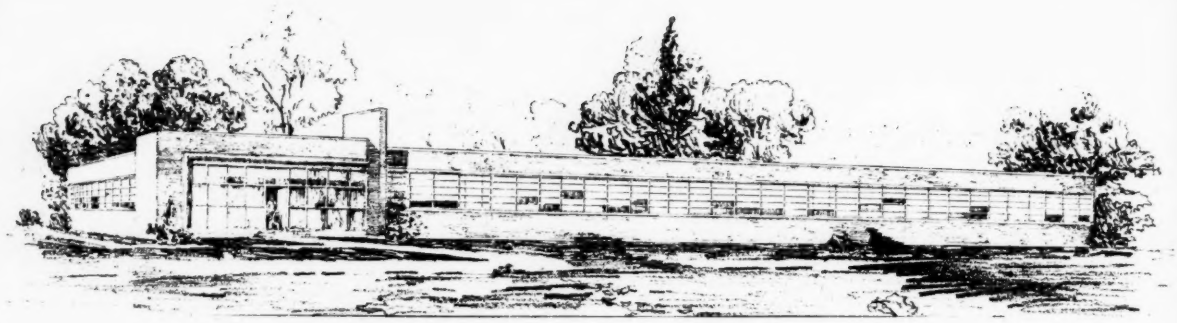
Aula Chemicals, Inc, continues to expand its line of pigment printing colors with the introduction of the 3000 series.

Since the granting of four patents in 1953 and '54 covering the use of water-dilutable pigment printing colors to Laszlo Auer, president of Aula Chemicals, the company has brought forth a rapid succession of products important to the textile printer: the 7000 series of highest grade pigment colors, the 100 series of low-cost extender clears, and the Aulabrite 900 series Hand Rub Washfast Extender Clears.

The new 3000 series, according to Leslie L Balassa, Aula vice president, represents many months of research and development around the experience gained in earlier work with water-dilutable pigment colors. The objective was to formulate a series that would offer brilliant shades and superior fastness properties without restrictions as to types of textiles. The result, according to Aula, is that the 3000 Series is comparable in fastness, brilliance and strength to the 7000 Series, while effecting a considerable saving to the user. Part of this result stems from the use of newly developed binders and dispersing agents. A further advantage of the 3000 line is its adaptability for use in the Aulabrite Hand Rub Washfast System.

It is reported that the new series has been enthusiastically received in limited production, and is now being produced for the general market.

Further information may be obtained from the manufacturer, Aula Chemicals, Inc, Box 494 (or 714 Division St), Elizabeth, N J.



Artist's conception of new laboratory for Fabric Research Laboratories in Dedham, Mass.

• Ground Broken for New FRL Lab

Fabric Research Laboratories, Inc, Boston textile research and consulting organization, has broken ground for a new laboratory and office building in Dedham, Mass. The building, of modern red brick construction, will contain 16,000 square feet of laboratory and office space, and will be located in Dedham at the junction of Routes 1 and 128, approximately 10 miles from downtown Boston.

The office wing will contain a lobby, administrative and staff offices and conference rooms. In the laboratory wing will be found the library, luncheon and recreational facilities, physical, chemical, microscopical and analytical laboratories, pilot plant, and shop. The entire building will be air conditioned.

Fabric Research Laboratories, Inc, was organized in 1942. Ernest R Kaswell is president, Kenneth R Fox and Milton M Platt, vice presidents, and Walter J Hamburger, treasurer. Its current staff numbers 40 scientists and engineers, under the direction of Dr Hamburger, with Messrs Kaswell, Fox, and Platt, associate directors, and George Thomson, assistant director.

The new building was designed by Chauncey C Chu, a senior research associate at Fabric Research Laboratories, Inc. Krokyn and Browne of Boston are the architects, and Canter Construction Company of Brookline, Mass, the builder. Occupancy is expected in March 1955.

• MCA Winter Conference

The 4th semi-annual meeting and winter conference of the Manufacturing Chemists' Association, which represents over 90% of the chemical industry's productive capacity, will be held at the Hotel Statler, New York, N Y, on Tuesday, Nov 23. The meeting will feature eight panel discussions on management topics of current and special interest to chemical industry executives.

• NETF Reports Gifts Totalling $12,035

Ralph K Hubbard, general chairman of the New England Textile Foundation's 1954 campaign for the benefit of New England textile colleges, reports that gifts totalling $12,035.00 had been received as of October 1st. The figure represents approximately 26% of NETF's announced goal of $45,000, which is needed in 1954-55 to pay for 53 scholarships, two fellowships and other expenses.

• GDGA Supporting PTI Fellowship

The Garment Dyers Guild of America has taken out a fellowship at the Philadelphia Textile Institute, thereby making available to its members the research facilities of the Institute.

Both broad general technical problems, as well as individual cases of dyeing difficulties will be handled for the Guild by PTI under this arrangement.

• CTS Papers Available

Papers presented at the recent Fourth Canadian Textile Seminar (over 30 in all) are now available in book form at $5.00 per copy to purchasers in the U S and Canada. Write to: The Textile Technical Federation of Canada, 1410 Guy St, Montreal 25, Que.

GENERAL CALENDAR

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS
Southern Textile Conference—Nov 4-5, North Carolina State College, Raleigh, N C.

AMERICAN SOCIETY FOR QUALITY CONTROL
Annual meeting, Textile Div—Jan 27-29, Clemson College School of Textiles.

DELTA KAPPA PHI FRATERNITY
1955 Annual Convention—April 29-30, Lowell, Mass.

DEUTSCHE GESELLSCHAFT FUR CHEMISCHES APPARATEWESEN
Achema XI—May 14-22, Frankfurt am Main, Germany.

DRYSALTERS CLUB OF NEW ENGLAND
Jan 24, April 29 (Hotel Vendome, Boston, Mass); June 24 (Outing—Wachusett Country Club, W Boylston, Mass).

THE FIBER SOCIETY
Spring Meeting—May 4-5, 1955, Alabama Polytechnic Institute, Auburn, Alabama.

Fall Meeting—Sept 8-9, 1955, Massachusetts Institute of Technology, Cambridge, Mass.

INTERNATIONAL TEXTILE EXHIBITION
2nd Exhibition—June 25-July 10, 1955, Brussels, Belgium.

INTERNATIONAL WOOL TEXTILE RESEARCH CONFERENCE
September, 1955—Sydney, Melbourne, and Geelong, Australia.

MANUFACTURING CHEMISTS' ASSOCIATION
4th Semi-annual meeting and Winter Conference—Nov 23, Hotel Statler, New York, N Y.

NATIONAL ASSOCIATION OF HOSIERY MANUFACTURERS, KNITTED OUTERWEAR ASSOCIATION, THE UNDERWEAR INSTITUTE
42nd Knitting Arts Exhibition—April 25-29, Convention Hall, Atlantic City, N J.

NATIONAL COTTON COUNCIL OF AMERICA
Annual Meeting—Jan 31-Feb 1, Hotel Shamrock, Houston, Tex.

Cotton Research Clinic—Feb 16-18, Pinehurst, N C.

NATIONAL INSTITUTE OF DRYCLEANING
4th Educational Conference—Dec 5-10, Silver Spring, Md.

NEW YORK PIGMENT CLUB
Nov 10, Dec 9, Jan 15.

TEXTILE RESEARCH INSTITUTE
25th Annual Meeting—March 10-11, Hotel Commodore, New York, N Y.

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